The Crystal and Molecular Structure

of

3.4;5.6 Dibenzphenanthrene

and

Decamethylene Glycol

THESIS

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Preface

This thesis describes research in chemical crystallography that was carried out during a three year period in the Chemistry Department of the University of Glasgow. It is expected that the work will be published.

I wish to express my sincere thanks to Professor J. Monteath Robertson for suggesting the problems for study and for his continued interest and guidance. During the past session I have received much valuable assistance from Dr. V. Vand. I am indebted also to Professor R. Pepinsky of Pennsylvania State College for an investigation of the structure of 3.4;5.6 dibenzphenanthrene using the X-ray Analogue Computer.

To the University of Glasgow I owe thanks for maintenance grants and especially for the awarding of a Coats Fellowship.

Summary

Described in the thesis are the results of research on four problems. In the main section the crystal and molecular structure of two compounds, 3.4;5.6 dibenzphenanthrene and decamethylene glycol, are reported. In the appendix is described work on the structure of decamethylenediamine, and on the precise determination of the cell dimensions of naphthalene. The two latter problems could not be completed.

3.4;5.6 Dibenzphenanthrene, $C_{22}H_{14}$, is of interest because of the intramolecular overcrowding present in its structure. It is monoclinic prismatic, C_{2h}^{6} - A2/a, with a = 26.17 A., b = 8.94 A., c = 19.57 A., and β = 105.1°. There are twelve molecules in the unit cell. The projection on (010) has been refined by Fourier and difference syntheses. The third co-ordinates of the atoms were obtained by trial and error from the (hk0) and (0kl) reflexions and are less accurate. The molecule is non-planar, the closest intramolecular approach of non-bonded carbon atoms being 3.0 A. The accuracy of the structure determination does not approach that usually obtained with aromatic hydrocarbons. However the nature of the molecular distortion has been demonstrated.

Decamethylene Glycol, $C_{10}H_{22}O_2$, was investigated to obtain further information about the alternation of carbon-carbon bond lengths in linear aliphatic compounds. This glycol is monoclinic prismatic, C_{2h}^5 - $P2_1/a$, with $a = 21.52$ A., $b = 5.21$ A., $c = 4.99$ A. and $\beta = 97.1^\circ$. There are two molecules in the unit cell. The structure was refined by Fourier syntheses using the (hk0) and (h0l) reflexions. In only the (001) projection are all the atoms clearly resolved. After correction for the termination of series error there was an average difference between alternate carbon-carbon bonds of 0.07 A. This difference is greater than that in hexamethylenediamine and in sebacic acid. It resembles the latter compound in the relative positions of the long and short bonds. Decamethylene glycol forms a layer structure. The contents of each layer are linked by hydrogen bridges of 2.83 A. length. A pronounced cleavage is observed parallel to the layers.

Appendix

Decamethylenediamine, $C_{10}H_{24}N_2$, was examined to gain further data on the alternation of carbon-carbon bond lengths such as had been found in the homologue, hexamethylenediamine. Like hexamethylenediamine, decamethylenediamine is orthorhombic dipyramidal,

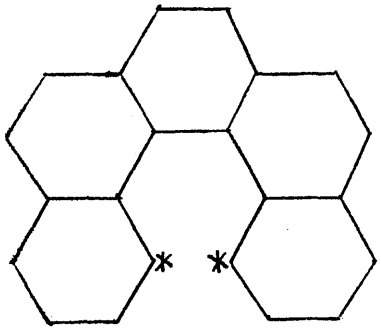
with space group D_{2h}^{15} - Pbca. The unit cell dimensions are a = 7.25 A., b = 5.72 A. and c = 29.4 A. There are four molecules in the unit cell. The crystals obtained were very thin blades which reacted with the carbon dioxide of the atmosphere. Due to the crystal dimensions and the need for protection during experimental work it has not been possible to obtain intensity data suited to a precise structure determination. However a correlation has been found between measured and calculated (0kl) structure factors. The molecular orientation is similar to that of hexamethylenediamine. It was not possible to refine the atomic co-ordinates found. Work on the problem was suspended when it was found that the analogous compound, decamethylene glycol was more suited to investigation.

An unsuccessful attempt was made to obtain precise axial lengths for the hydrocarbon naphthalene using the Straumanis technique. With Copper K_α radiation the high orders of the axial reflexions were either very weak or not observable. This fundamental difficulty is likely to be present in other low melting organic compounds.

The Crystal and Molecular Structure of 3.4;5.6 Dibenzphenanthrene

Introduction

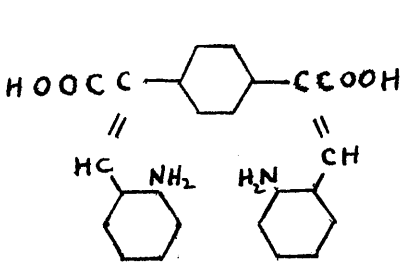
3.4;5.6 Dibenzphenanthrene is interesting from the structural point of view because the atoms in the starred positions cannot be as close together as the conventional formula might indicate.



The molecular overcrowding at this point must result in the molecule assuming a non-planar configuration (11). That the substance is non-planar has been demonstrated by the resolution of the optical isomers of 3.4;5.6 dibenzphenanthrene 9.10 dicarboxylic acid (3). Numerous investigations have shown that aromatic hydrocarbons form coplanar systems (naphthalene, anthracene, coronene and others). Nevertheless 3.4;5.6 dibenz-

-phenanthrene has the properties of an aromatic hydrocarbon. It is thus of importance to determine the exact nature of the molecular distortion.

In the synthesis of 3.4;5.6 dibenzphenanthrene(10) $\alpha\alpha$ bis-o-aminobenzal-p-phenylene-diacetic acid (I) is diazotized and by treatment with copper powder, ring closure is induced. Two products are formed; the planar 1.2;5.6 dibenzanthracene 4.8 dicarboxylic acid (II) and the non-planar 3.4;5.6 dibenzphaneathrene 1.8 dicarboxylic acid (III).



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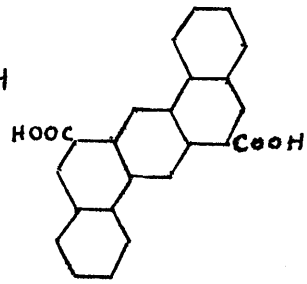

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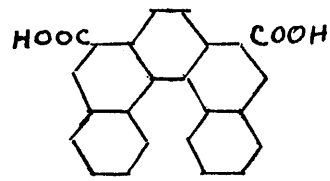

III

The separation of the two products is difficult and the description of the syntnesis does not give the exact yield of each. But the non-planar product is formed in considerable quantity.

The crystals employed in the structure determination were kindly supplied by Professor J.W. Cook. They were yellowish bipyramids with well developed

faces. When the problem was commenced work already had been done on it (36). The unit cell dimensions and the space group had been determined but the density was not known.

Crystal Data

3.4;5.6 Dibenzphenanthrene, $C_{22}H_{14}$; M, 278.3 ; m.p. 177-178°C ; d calculated 1.253, found 1.264. Monoclinic prismatic,

$a = 26.17 \pm 0.15$ A., $b = 8.94 \pm 0.03$ A., $c = 19.57 \pm 0.07$ A.

$\beta = 105.1 \pm 0.3°$

Absent spectra, (h0l) when h is odd and l is odd, (hkl) when k+l is odd. Space group C_{2h}^6 - A2/a. Twelve molecules per unit cell. Possible molecular symmetry, a two-fold axis. Volume of the unit cell = 4419 A^3. Absorption coefficient for X-rays ($\lambda = 1.542$ A.) $\mu = 6.6$ $cm.^{-1}$. Total number of electrons per unit cell = $F_{(000)} = 1752$.

Experimental

The crystals of 3.4;5.6 dibenzphenanthrene have well developed faces so that it is possible to set them by optical methods to rotate about the b crystallographic axis. The a and c axes are not represented

by main zones of faces so that setting had to be by trial. Rotation, oscillation and zero layer Weissenberg moving film photographs were taken of crystals rotated about the three main axes. Rotation and oscillation photographs were taken also about the diagonal of the ac plane. This is the axis of a main zone of faces. In addition Weissenberg photographs were taken of the (n1l) and (n2l) layers of the reciprocal lattice. Copper radiation filtered through nickel foil (λ = 1.542 A.) was used throughout. Oscillation photographs showed that there was only one symmetry axis, which was designated the b crystallographic axis. The zero layer moving films demonstrated that the $a \wedge b$ and $b \wedge c$ interaxial angles were right angles. The $a \wedge c$ angle is $105.1 \pm 0.3^{\circ}$. The crystal is monoclinic. The rotation photographs permitted the calculation of the axial lengths.

$$a = 26.17 \pm 0.15 \text{ A.}$$

$$b = 8.94 \pm 0.03 \text{ A.}$$

$$c = 19.57 \pm 0.07 \text{ A.}$$

These values are in agreement with those of White (36). a = 25.8 A., b = 8.91 A., c = 19.51 A. $\beta = 105.0^{\circ}$.

The a axis rotation photograph is reproduced in Figure 1.

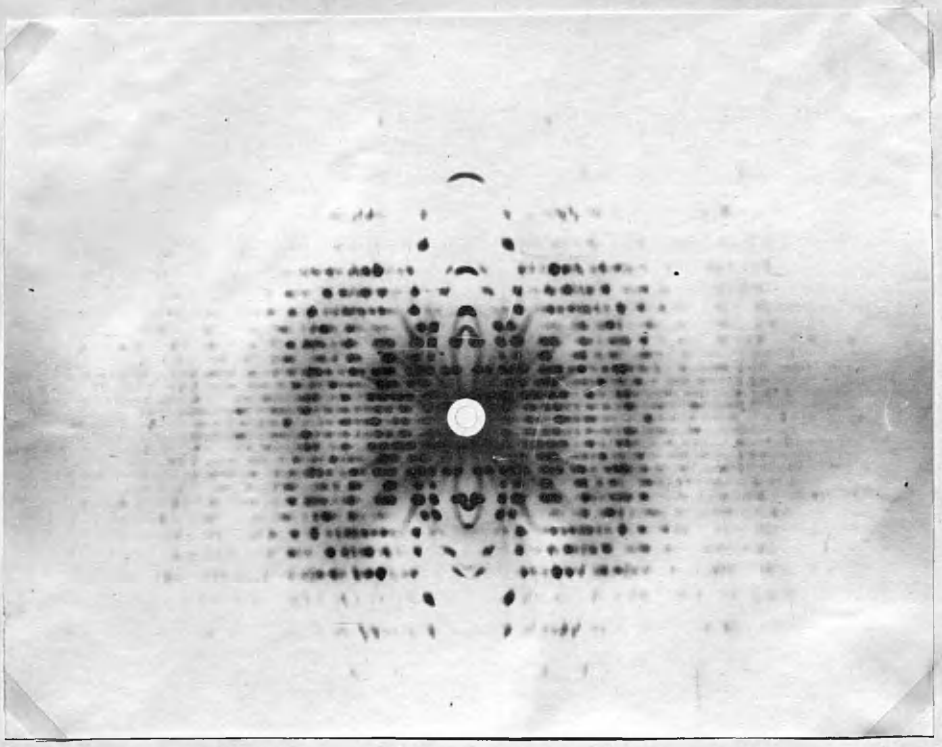

Figure 1. Rotation photograph, a axis 3.4:5.6 dibenzphenanthrene. Copper radiation (λ=1.542 A.)

By flotation in aqueous calcium chloride solution the density was found to be 1.264. The calculated density assuming twelve molecules per unit cell is 1.253.

When the moving films were indexed it was found that (n0l) reflexions are absent when n is odd and l is odd. General reflexions (nkl) are absent when k+l is odd. These absences indicate a glide plane of translation a/2 and an A end centred cell.

In the monoclinic system there are two space groups with these symmetry relations; C_s^4 - Aa, monoclinic domatic and C_{2h}^6 - A2/a, monoclinic prismatic. The former space group does not have a centre of symmetry. Since there are twelve molecules in the unit cell the space group with the higher symmetry seemed more probable. The structure analysis was begun using this assumption.

Later as a check on the choice of space group a survey of the distribution of the intensities was made. Wilson (37) has shown that the distribution should be different for centrosymmetric and non-centrosymmetric space groups. The Wilson ratio was calculated for the (h0l) and (hk0) intensity data. Reflexions too weak to

be observed were assigned an intensity half that of the minimum observable value. The results were inconclusive. The variation of Howells, Phillips and Rogers (16) was then tried. The plot of the N(z) function for the (h0l) and (hk0) intensities is shown in Figure 2. It can be seen that the distribution compares best with the theoretical curve for a centrosymmetrical structure. The (h0l) data are more extensive and this no doubt accounts for the smoother curve obtained in this case.

Since the crystals have well developed faces some goniometric measurements were made using a Unicam X-ray spectrometer. When rotated about the b crystallographic axis two sets of equivalent faces were found. The interfacial angles were $44^{\circ}23'$ and $135^{\circ}37'$. When the crystal was rotated about the ac diagonal (identified by its rotation photograph) a small face was observed parallel to the symmetry plane of the crystal. The interfacial angles between this and the two neighbouring faces in the zone were $117^{\circ}9'$. From these measurements the faces in the (h0l) zone were identified as (100) and (101). In the axial zone the faces were (010) and $(11\bar{1})$.

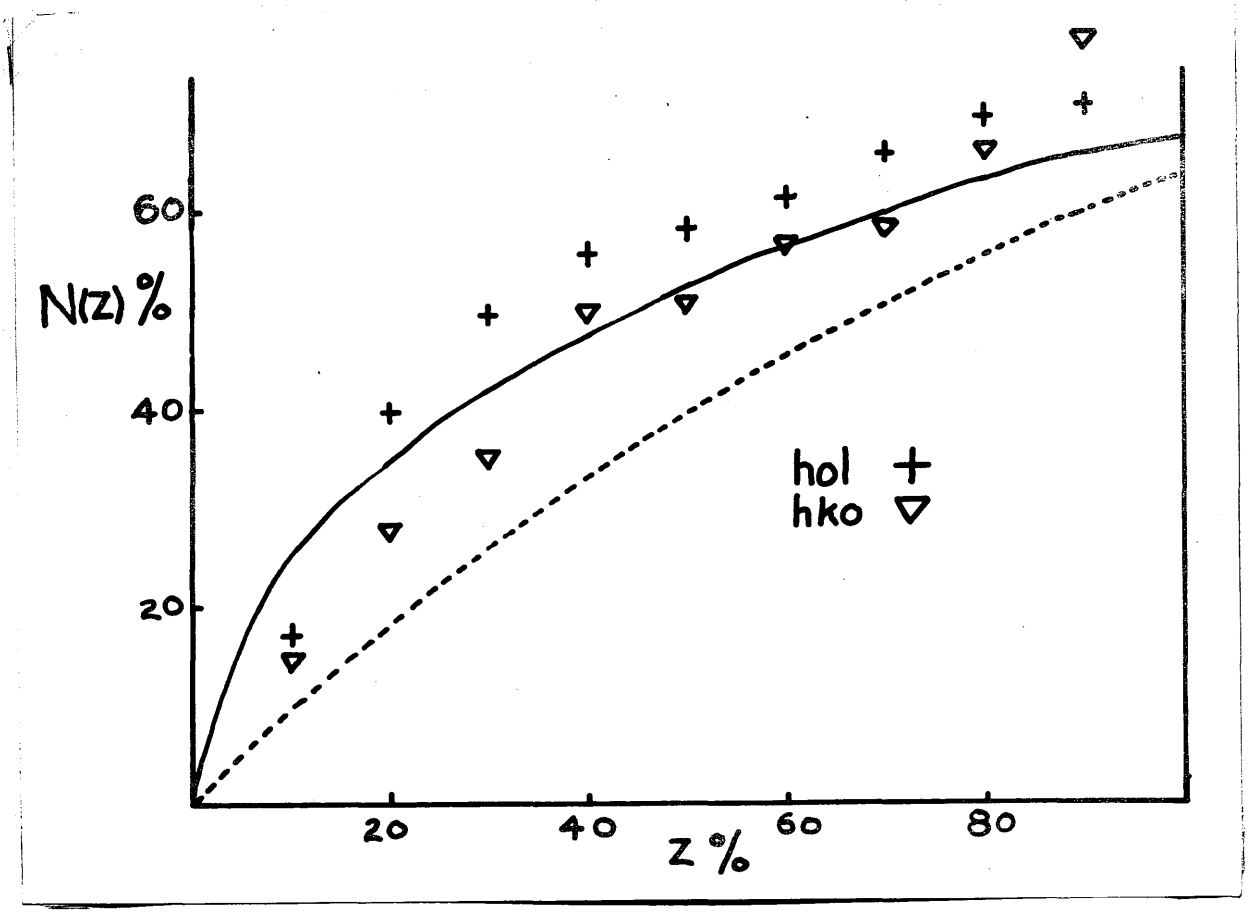

Figure 2. Distribution of (h0l) and (hk0) intensities, 3.4;5.6 dibenzphenanthrene. z is the percentage of the mean intensity. N(z) is the percentage equal to or less than z. Full curve is the theoretical distribution for a centrosymmetric structure, broken curve for non-centrosymmetric.

The faces observed are consistent with a centrosymmetric structure. A sketch of the crystal is shown in Figure 3.

The intensity data were obtained from zero layer Weissenberg photographs taken about the b and c crystallographic axes. The reflexions were recorded up to the limit for copper radiation. The multiple film technique (25) was used to correlate strong and weak intensities. Visual estimation of intensities was employed. For both the (n0l) and (nk0) zones the crystal cross sections were 0.5 by 0.4 mm. To increase the range of intensities from the (n0l) zone larger crystals 1.0 by 0.8 mm and 1.2 by 0.7 mm were employed. The large crystals were used only for the weak reflexions. The crystals were entirely immersed in the X-ray beam. The range of intensities covered was 5500:1 for the (h0l) zone and 2500:1 for the (hk0) zone. The intensities were not corrected for absorption, the difference caused by the irregular shape not being sufficient to warrant it.

The intensities were corrected by the Lorentz-polarization factor, the resulting value being considered equivalent to a relative F^2 assuming the crystal to be ideally imperfect.

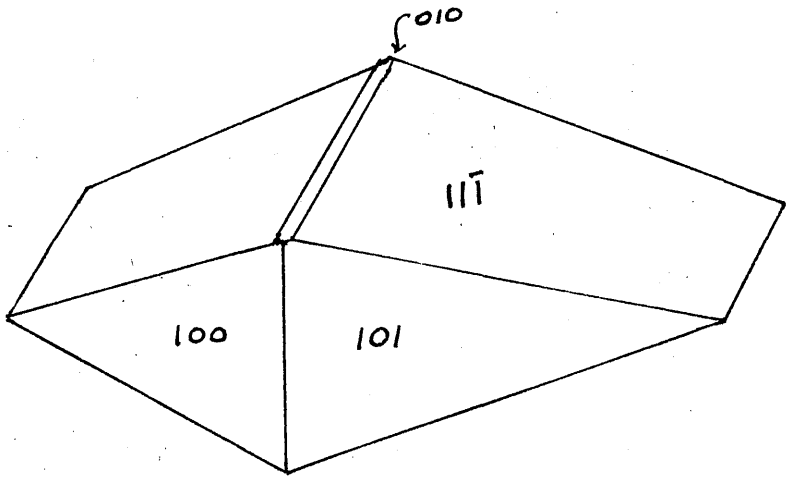

Figure 3. Sketch of crystal of 3.4;5.6 dibenzphenanthrene.

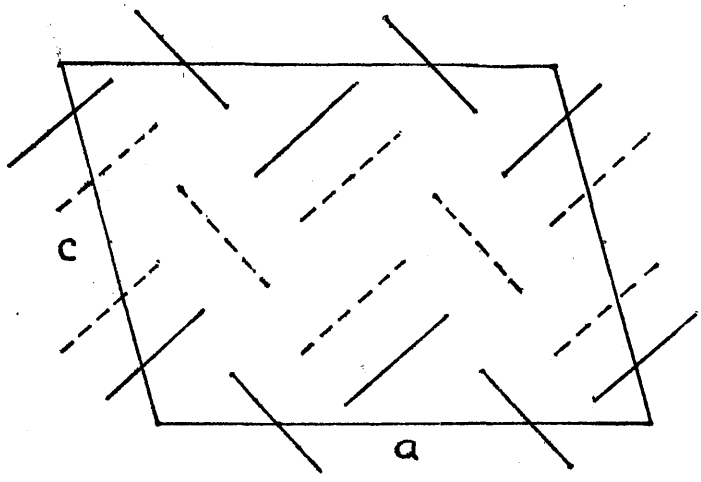

Figure 4. Relative positions of molecules in the unit cell of 3.4;5.6 dibenzphenanthrene.

The structure factors from the (0kl) zone that were employed in the analysis were obtained from an ordinary moving film. Thus the accuracy of these will be lower than in the case of the intensities from the other two zones.

In the calculation of the Fourier and difference syntheses for the (h0l) zone the two axes were divided into 60 divisions. Three figure numerical methods (27) were used for all except four of the difference syntheses. These were calculated using the Vand mechanical computer (33). The structure factor calculations were done numerically employing two figure trigonometric tables.

Analysis of the structure

General

The size of the unit cell with its content of twelve molecules increased considerably the difficulty of solving the structure. It became evident from the first that the projection down the short b axis would be the only one with much hope of resolution.

The space group A2/a has eight general positions and five sets of four-fold special positions (17). Since there are twelve molecules in the unit cell the

asymmetric unit must be either three or one and a half chemical molecules. It was suggested that the twelve molecules might be distributed among the eight general positions and four special positions. Occurrences of this type of distribution are recorded for biphenylene (35) and dibiphenylene ethylene (14).

Of the sets of special positions four require the molecule to have a centre of symmetry and the fifth requires a two-fold molecular axis. The latter is the only type of molecular symmetry possible. Thus there would be eight molecules in general positions and four in special positions, the latter using their two-fold axes of symmetry. The asymmetric unit would then be one and a half molecules. There would be molecules at the eight equivalent general positions;

$x\ y\ z$; $\bar{x}\ \bar{y}\ \bar{z}$; $\frac{1}{2}-x,\ y,\ \bar{z}$; $\frac{1}{2}+x,\ \bar{y}\ ,\ z$;

$x,\ y+\frac{1}{2},\ z+\frac{1}{2}$; $\bar{x},\ \bar{y}+\frac{1}{2},\ \bar{z}+\frac{1}{2}$; $\frac{1}{2}-x,\ y+\frac{1}{2},\ \bar{z}+\frac{1}{2}$; $\frac{1}{2}+x,\ \bar{y}+\frac{1}{2},z+\frac{1}{2}$.

The four molecules in special positions would have their two-fold axes parallel to the b crystallographic axis and located at the equivalent points; $\frac{1}{4},y,0$; $\frac{3}{4},\bar{y},0$; $\frac{1}{4},\ y+\frac{1}{2},\ \frac{1}{2}$; $\frac{3}{4},\ \bar{y}+\frac{1}{2},\ \frac{1}{2}$.

The structure analysis was commenced on this assumption.

An inspection of the three zero layer moving films

showed that the intensities of the (n0l) zone were on the average much stronger than those of the other two zones. The maximum observed structure factor in the (n0l) zone is 294, the maximum in the (hk0) zone is 97 and in the (0kl) 134. Of the (h0l) reflexions the (h0$\bar{h}$) series is the most intense with the (h0h) reflexions of somewhat lower value. The (n00) reflexions are of medium intensity and the (00l) ones are very weak. This indicated that the thickly populated directions in the crystal were, in projection, parallel to the two diagonals of the ac plane. It was noted that among the strong planes of moderately high order were; (10,04), (14,04) (8,0$\bar{1}$0) and (10,0$\bar{1}$0). These too are diagonal planes. The symmetry requires that the molecules in the special position lie with their two-fold axes perpendicular to the (010) crystal face. Packing considerations then require that the molecules in the general position should be arranged with their axes at least nearly in the same direction. The observation that the (h0l) intensities are more intense than those in the other two zones now is reasonable. In the projection down the b crystallographic axis the molecules would be viewed edgewise and thus there would be a higher concentration of scattering matter than in the other two zones.

To simplify the structure factor computations an asymmetric unit was chosen in the middle of the unit cell. This avoided negative values for the atomic co-ordinates. When the analysis was completed the co-ordinates were transformed to a position at the origin.

The location of the two parts of the asymmetric unit was based on a consideration of the strong reflexions. It was found by trial that the molecule in the special position must lie almost parallel to the trace of (402). The molecule in the general position would then lie almost on the trace of $(10,0\bar{1}0)$. To limit further the position of the molecule in the general position use was made of the strong reflexions (00,12) and (015). The structure factor of (00,12) has maxima when the two-fold axis of the molecule in the general position lies at $360x/a = 150^{\circ}$, 165°, 180° etc. Packing considerations limit this to 165°. The corresponding z co-ordinate is 111°. At this position the structure factor of (00,12) is at a positive maximum. The structure factor function of (015) is of the $\cos 2\pi ky . \cos 2\pi lz$ type. When a graphical representation of this is superimposed upon a molecular model it can be seen that maxima occur when the two-fold axis of the

molecule in the general position is at $360z/c = 72^\circ, 108^\circ, 144^\circ$ etc. Packing limits this to 108°. The corresponding x co-ordinate is 162°.

The strong reflexion (015) also gives information regarding the distortion of the molecule. Due to the form of the structure factor function for this reflexion it is not possible for a planar configuration of the carbon atoms to provide a high calculated value. The direction of the distortion was obtained in this manner. Later in the analysis it was found that the sense of the distortion thus obtained was correct only for the molecule in the general position.

Approximate y co-ordinates for the carbon atoms were obtained from a consideration of the strong (080) reflexion. This structure factor has maxima at positions corresponding to the distance between rows of carbon atoms in the molecule. The other reflexions of the series (0k0) and (015) also were used.

For positioning the asymmetric unit much use was made of graphical representations of the structure factor function (26),(13). These were drawn out as required for the strong reflexions. In the (h01) zone the structure factor has the form $\cos 2\pi(hx+lz)$. The maxima can be

represented by a series of parallel straight lines cutting the a and c axes at multiples of a/h and c/l respectively. In the other two main zones the function is in the form of a product cos $2\pi A.\cos 2\pi B$ or $\sin 2\pi A.\sin 2\pi B$. These functions change sign at positions given graphically by the lines of a grid.

With co-ordinates chosen from the above considerations and assuming a carbon-carbon bond length of 1.41 A. work was begun on devising a trial structure. After many trials a moderately reasonable one was found. Structure factors (65 in number) from the main zones were then calculated. Of these 50 were from the (h0l) zone. A composite scattering curve for hydrocarbons (24) was employed in the calculations. The contribution of the hydrogen atoms was neglected. The discrepancy for this set of structure factors calculated as $100.\Sigma||F_m| - |F_c|| / \Sigma|F_m|$ was 40%.

During the process of refining the structure the discrepancy has been calculated on an increasingly large number of structure factors. This omission of the calculation of all the structure factors for each stage of the refinement reduced the labour of computation. However it does not permit a direct comparison between all the postulated structures.

The packing of the molecules in the unit cell is shown diagrammatically in Figure 4. The distortion is not indicated. Broken lines represent molecules translated y/2 from those with full lines.

Refinement of the (h0l) zone.

Attention was concentrated on the (h0l) zone because it seemed the most favourable to solution. Many attempts were made by trial and error to improve the discrepancy but without success. In these trials only moderate distortion of the molecule was postulated.

A Fourier projection down the b crystallographic axis was next calculated, using 41 terms of which the signs could be ascertained with fair certainty from the calculated structure factors. It was hoped that some clue to the distortion might come from this Fourier. It gave resolution of only groups of atoms. It did indicate however that the molecule in the special position had been assigned a distortion in the wrong direction. The atomic positions were adjusted to satisfy the peaks in the Fourier projection and another set of structure factors were calculated. The cycle was repeated twice more with larger numbers of terms. The discrepancy for a standard

set of 77 structure factors decreased by approximately 10% during the process.

A composite of the third Fourier projection is shown in Figure 5. Much irregular detail exists near the edges of the projected molecules. Attempts at placing atoms according to these auxilliary peaks did not lead to any improvement of the discrepancy.

At this stage in the analysis an opportunity arose by which the data for the (h0l) zone were submitted to an analysis by the X-ray Analogue Computer at Pennsylvania State College. This work was done by Professor Robertson and Professor Pepinsky but an account of it is given here to complete the continuity of the structure determination. It did not provide a solution to the problem but it did give a density distribution qualitatively similar to the one finally obtained.

The X-ray Analogue Computer is a mechanism designed by Pepinsky (21) for electronically synthesizing Fourier projections. The structure factor values and the appropriate phase angles are set into the machine and these are summed, the resulting electron density distribution being displayed on a cathode ray oscilloscope.

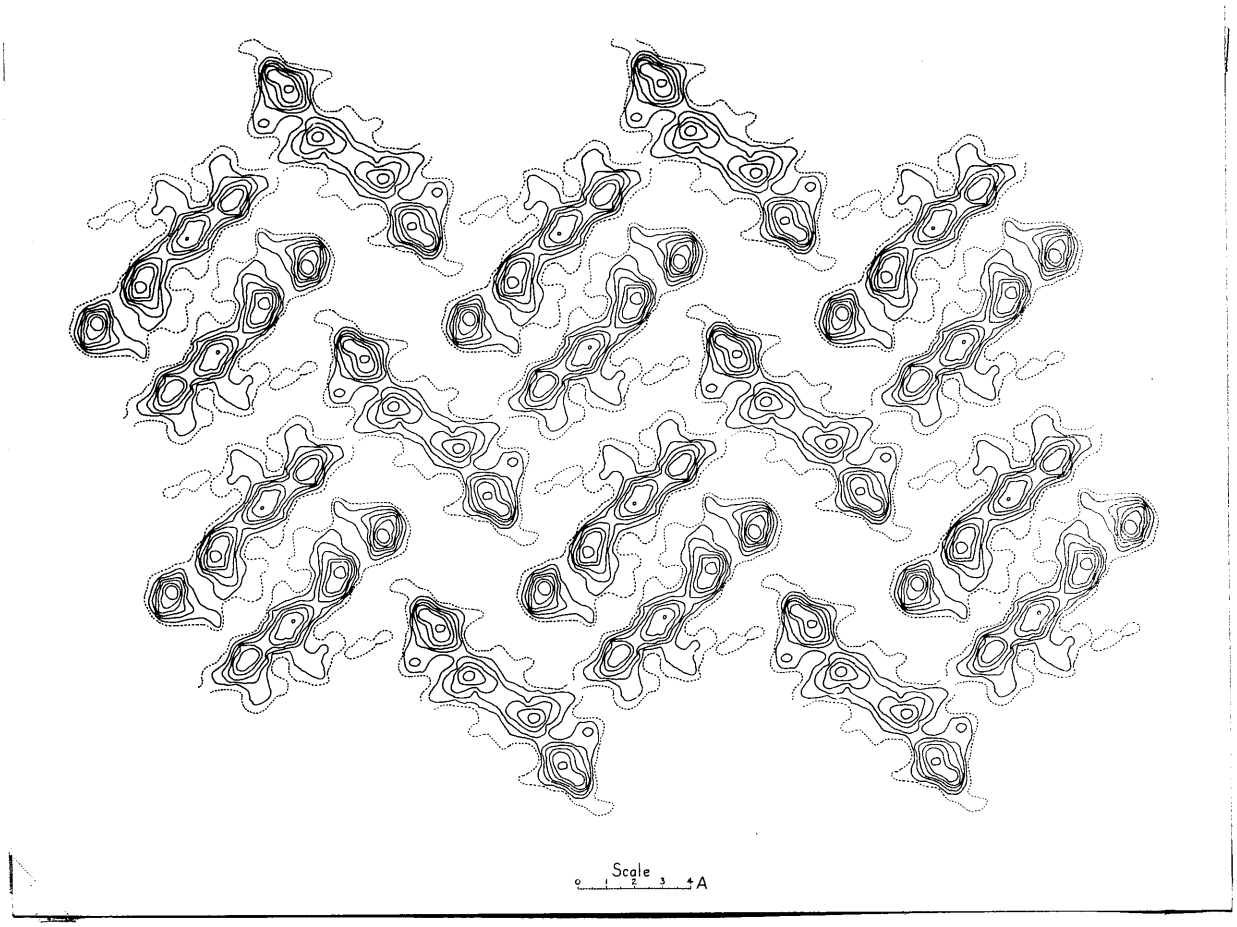

Figure 5. Dibenzphenanthrene molecules projected on (010). Based on third Fourier synthesis.

By appropriate circuitry the contour lines representing the electron density are shown. A grid also can be superimposed over the Fourier synthesis. The computer has the advantage that the phases of the terms may be changed at will. By suppressing the main contour lines only the background can be left visible. If the Fourier correctly represents the structure the background should be uniform. This provides a criterion for the correct choice of phase angles. The final Fourier projection from this investigation (obtained by Professor Pepinsky) is shown in Figure 6. It is to be noted that the areas bordering molecules have well developed detail. It is in this respect that this projection differs from Figure 5. I am indebted both to Professor Robertson and to Professor Pepinsky for this investigation of the structure.

When co-ordinates were chosen from the photograph of the electronically computed Fourier and a set of structure factors were calculated no improvement in the discrepancy ensued. The choice of co-ordinates was difficult as there were no well resolved atoms.

It is possible that further progress might have been made in this direction but another mode of attack was tried. The method of error or difference syntheses was applied to the problem. A difference synthesis is

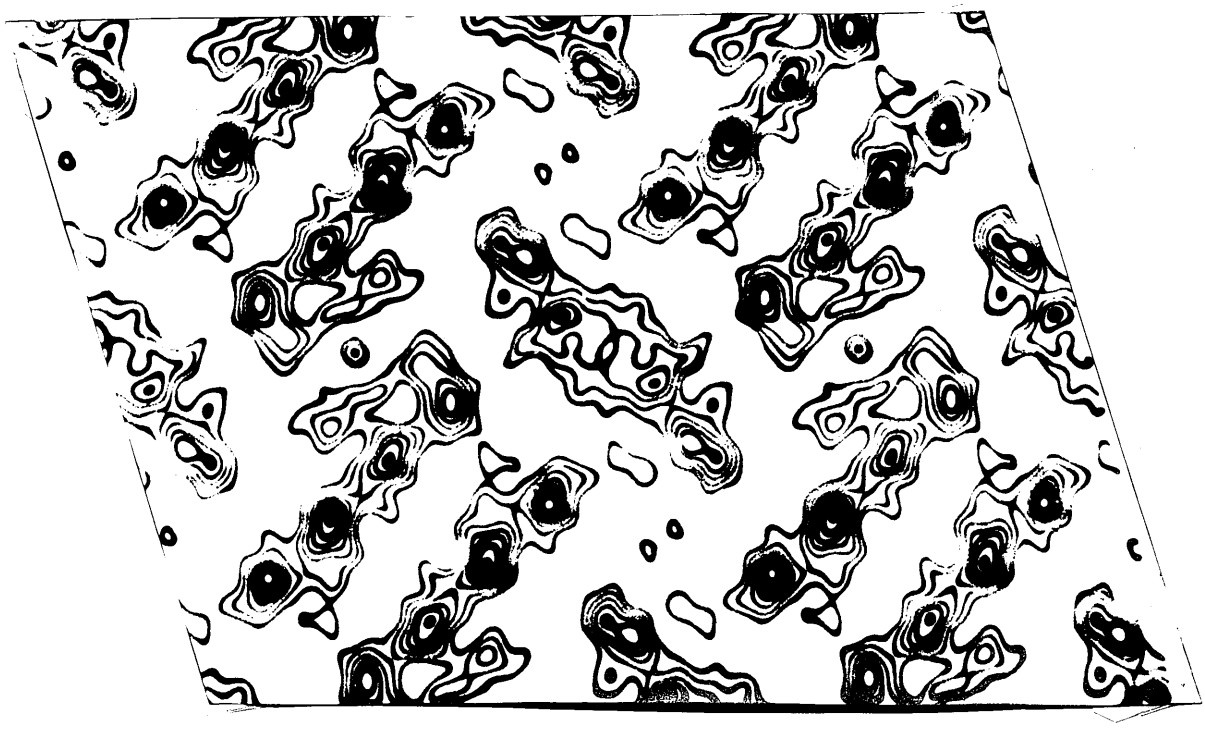

Figure 6. Projection of molecules of 3.4;5.6 dibenzphenanthrene on (010). From a photograph of the screen of the X-ray Analogue Computer. Synthesis by Pepinsky.

one using the value of $F_m - F_c$ as coefficients. It is in effect a Fourier synthesis (calculated in the normal manner) from which has been subtracted a Fourier, the coefficients of which are the F_cs. The method was used by Bunn (12) in the analysis of sodium benzylpenicillin. Booth (5) showed that the difference synthesis was equivalent to a form of the method of ' steepest descents'. It was employed also by Cochran (9) in the refinement of adenine hydrochloride. It can be shown that with a well resolved atom whose chosen co-ordinates are in error the difference synthesis will give two areas, one of positive and one of negative density. In order to minimize the difference between the calculated and measured value of the structure factors the atomic co-ordinates must be moved away from the negative area toward the positive area. From the known electron density profile of the atom (obtained from another finished structure) it is possible to calculate the atomic shifts. The difference synthesis has the property also of giving co-ordinates corrected for the termination of series error.

The present problem introduced difficulties not found in the usual structure analysis. There was a great deal of overlapping of atoms so that the slopes in the difference synthesis might refer to more than one

atom. In order to obtain a direct refinement the number of terms employed in the synthesis should be much larger than the number of parameters to be refined. In the present case the number of co-ordinates was 66 and the number of useable terms not normally above 100. It was not found possible to obtain the correct amount of the atomic shifts but usually the direction of the corrections was given.

A first difference synthesis was calculated from the structure factors obtained from the co-ordinates of the third Fourier. After consideration it was decided that the structure was unreasonable. It had been based on the density plot of the Fourier using co-ordinates that were at the centres of gravity of groups of atoms. A model of the structure composed of steel springs was distorted to fit the Fourier synthesis. A parallel beam of light was employed for the purpose of measuring the co-ordinates. The postulated distortion of non-bonded carbon atoms was about 2.4 A.

From these co-ordinates another set of structure factors were calculated. The discrepancy (for 77 reflexions) was 40½%. This was equivalent to the discrepancy of the discarded structure. A second difference

synthesis was computed using these results. The atomic positions were altered according to the contours of the synthesis and the structure factors were recalculated. The discrepancy decreased by only 0.7%.

A third difference synthesis was then calculated and the scale of the corrections was increased. The new co-ordinates of the carbon atoms obtained from this synthesis gave a set of structure factors with a discrepancy of 34%. The same 77 reflexions were included in the discrepancy calculation. The third synthesis is shown in Figure 7. The general tendency of the atomic shifts had been to spread out the molecule, increasing the amount of distortion. Positive areas were to be found at the sides of the molecules which themselves lay in troughs of negative density. Successive shifts had not removed this large negative area. It was suggested that this was caused by an incorrect scaling factor. The relative measured structure factors had been put on the same scale as the calculated by the use of the factor $\Sigma|F_c| / \Sigma|F_m|$. This treats all the structure factors as being equally accurate. A least squares method is more suited theoretically and the scaling factor then becomes $\Sigma|F_m F_c| / \Sigma|F_m^2|$. The use of this formula gave a scaling factor approximately 5% lower than that obtained from the

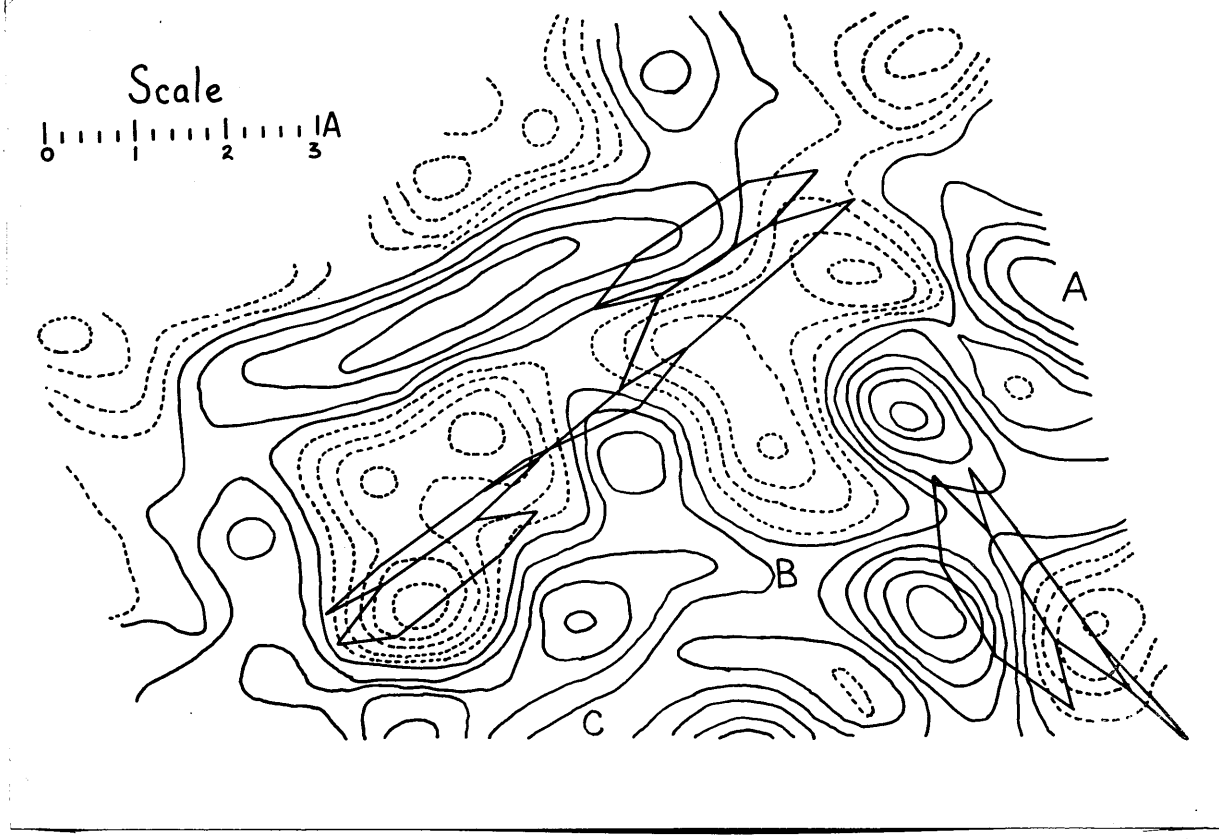

Figure 7. Third difference synthesis, dibenzphenanthrene. Projection on (010). Contours at intervals of 0.5 $e.A^{-2}$. Positive contours in full lines. The co-ordinates derived from the synthesis are shown.

conventional treatment.

Using the new scaling factor a fourth difference synthesis was calculated. Co-ordinates from this gave a set of structure factors with a discrepancy of 32½%. The calculation included the usual 77 structure factors.

In an attempt to increase the rate of the refining process a still larger number of structure factors were calculated. Attention was given to those reflexions that were either absent or very weak. When the co-ordinates are not correct these weak terms are likely to have a calculated value much higher than the measured one. The sign of the term in the difference synthesis is then known with certainty because the calculated structure factor must decrease. A fifth synthesis was computed using this larger number of terms. Co-ordinates obtained from the synthesis were used to calculate another set of structure factors which had a discrepancy of 31½% (for 77 reflexions)

Since the scaling factor had continued to decrease during the refinement an attempt was made to find a final value by extrapolation. The scaling factors were plotted against the number of syntheses and a smooth curve was drawn through the points. The value at a position equivalent to two syntheses after the current one was used. It is interesting to note that this value was

only slightly below the one from the final set of structure factors.

This scaling factor was then used to obtain the terms for a sixth difference synthesis. This resulted in a set of structure factors with the same discrepancy as before - 31½%.

A seventh difference synthesis reduced the discrepancy to 31%. The process of refinement seemed to have come to a standstill.

At this time the results of a mathematical analysis of refinement by difference syntheses became available (34). This indicated that the low order calculated structure factors must themselves be approximately correct before the refinement of the higher orders could be accomplished. In a qualitative sense this is due to the much smaller shifts required to change the signs of the high order structure factors. It was therefore desirous to exaggerate the effect of the low order terms of the synthesis. This was done by weighting the coefficients according to an empirical function which gave much greater weight to the low order terms. The result of the weighting was to make the high order coefficients negligibly small. Therefore they were omitted from the synthesis. Only coefficients with indices up to and including 8 were used in the eighth

synthesis.

In the eighth synthesis only two large positive areas appeared. Peaks corresponding to these but of smaller magnitude can be seen in the third difference synthesis at points A and B of Figure 7. The atomic co-ordinates were changed according to the indications of the synthesis and the structure factors were recalculated. The discrepancy was 25% for the 40 reflexions included in the calculation. It was estimated that the improvement compared to the previous synthesis was about 1½%.

A ninth synthesis was next calculated using the same number of weighted low order coefficients. The discrepancy from the new set of structure factors was still 25%.

The tenth synthesis made use of the same number of weighted low order coefficients. The shifts of the atomic co-ordinates in these weighted syntheses were made in the direction of the large peak at the position A, Figure 7. The exact amount of the shift was adjusted to make some of the strong structure factors approximately correct. These shifts were increasing unreasonably some of the carbon-carbon bond lengths. It was beginning to be realized that the strong peak in the weighted synthesis was spurious. It was situated at a point which was , in

projection, a centre of symmetry. However the discrepancy from the resulting set of structure factors was calculated and found to be 26% - a slight increase.

The eleventh synthesis was computed using only low order terms but no weighting was employed. Inspection of this synthesis showed another direction of shift that seemed capable of giving the same improvement of the discrepancy as the motion toward the large peak at A. The molecules were now well spread out and it appeared possible to make use of the graphical plots of the strong high order structure factors (26,0,$\overline{10}$) and (6,0,18). Until this time it had not been possible to obtain a structure consistent with these strong high order reflexions. From reference to the structure factor graphs a new position for one of the benzene rings of the molecule in the general position was devised. The change of co-ordinates was in the direction of the centre of symmetry at the point C, Figure 7. The configuration was designed to make both (26,0,$\overline{10}$) and (6,0,18) strongly positive. The motion of six of the atoms was drastic, some being shifted as much as 0.4 A The atoms which had been shifted toward the peak at A were now moved back to give reasonable carbon-carbon bond lengths. The structure factors were then calculated for all reflexions with indices up to and including 14. There

were 112 of these. The discrepancy was 36%. To form a comparison with the seventh synthesis the discrepancy for the same 77 structure factors was found. This was 32½% an increase of 1½%.

The twelfth difference synthesis made use of most of the 112 structure factors from the preceding calculation. The co-ordinates from this synthesis gave structure factors with a discrepancy of 27½% (for 112 reflexions). This was a decrease of 8½% which seemed to justify the changes made from the eleventh synthesis.

A fourth Fourier synthesis was now computed using 94 terms, some of uncertain sign being omitted. The Fourier gave fair resolution of the outer atoms of the molecules. However no success was experienced in improving the discrepancy using co-ordinates obtained from it.

As a result another difference synthesis, the thirteenth, was calculated . This contained 104 terms. In this synthesis there were two peaks which experience proved to be spurious. By a combination of trial and use of the contours of the synthesis a new set of co-ordinates was found. These gave structure factors with a discrepancy of 25½% (112 reflexions), a reduction of 2%.

The thirteenth synthesis is shown in Figure 8.

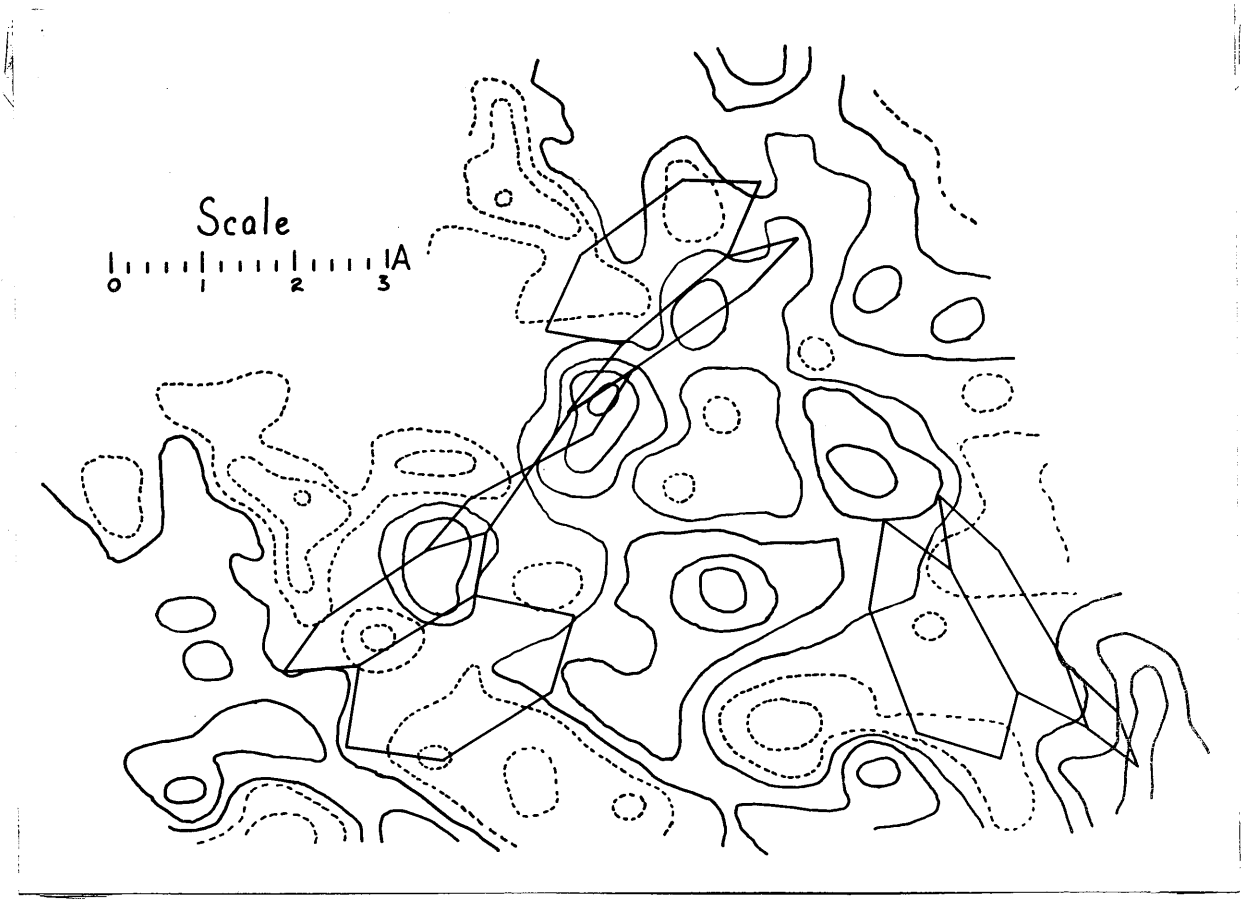

Figure 8. Thirteenth difference synthesis, dibenzphenanthrene. Contours at intervals of 0.5 e. $Å^2$. Positive contours in full lines. The co-ordinates derived from the synthesis are shown.

It can be seen that there is a marked change from the third synthesis. The large negative area in which the molecules lay has now disappeared.

An additional 47 structure factors were calculated. The discrepancy for 146 of the observed structure factors of the (h0l) zone is 27%. It can be seen that a measure of refinement has been brought about. The 159 structure factors that have been calculated for this zone are collected in Table 2. The calculation of all the theoretically possible structure factors (for copper radiation) is a task of considerable length and has not yet been attempted.

To provide a view of the electron density distribution of the structure in its present state of refinement a fifth Fourier synthesis was calculated, containing 121 terms. (Figure 9). Much of the detail is still obscured by the overlapping of atoms but the form of the molecular distortion is clearly visible.

Investigation of the (hk0) and (0kl) zones.

It remained to obtain the other co-ordinate of the carbon atoms. In the second and third main zones a projection would contain at least four superimposed molecules. It did not appear that a difference synthesis

Figure 9. Two molecules of dibenzphenanthrene projected on (010). Contours at intervals of 2 e.$\AA^2$, the two electron line being broken. The final co-ordinates are superimposed upon the density map.

would give much help. A method of trial and error was used but this does not permit refinement when applied to such a large asymmetric unit.

It was assumed that the average carbon-carbon bond length was 1.45 A. Using this value the y co-ordinates with respect to an arbitrary position were found from the tilt of the molecule. These values of the y co-ordinate then had to be translated by amounts sufficient to give correlation between calculated and measured (hk0) and (0kl) structure factors. Since there are two unrelated parts to the asymmetric unit there are several possible positions. Use was made of the series of axial reflexions (020), (040), (060), (080) and (0,10,0). These are relatively simple to calculate. The original trial structure had been designed to satisfy (hk0) and (0kl) measured structure factors but the great change in the distortion of the molecule required revision to be made. The (080) structure factor is at approximately 45% of its possible maximum. This limits drastically the positions that the molecules may occupy. When general agreement had been attained using the axial reflexions attention was turned to two strong high order structure factors (18,2,0) and (16,4,0) and to the series of the other zone (011), (013), (015) and (017). After numerous trials a reasonable correlation was found for the limited

number of structure factors employed. In this configuration of the asymmetric unit the two-fold axis of the molecule in the special position points in the reverse sense to that of the molecule in the general position. The correlation is given below.

hkl	F_m	F_c
020	56	-56
040	39	41
060	12	-29
080	97	99
0,10,0	<12	-8
18,2,0	66	75
16,4,0	65	-72
011	95	-96
013	51	-46
015	134	124
017	33	29

When all the 62 observed structure factors of the (hk0) zone were calculated the discrepancy was 44½%. Further attempts at refinement have not been made.

Some additional structure factors of the (0kl) zone have been computed. The agreement is reasonable.

The structure factors of these two zones are listed in Table 2.

Co-ordinates, Dimensions and Orientation

The co-ordinates of the carbon atoms are listed in Table 1. The origin is at a centre of symmetry. The co-ordinates x, y and z are expressed as fractions of

Table 1. Co-ordinates of the carbon atoms of 3.4;5.6 dibenzphenanthrene

Atom	x	y	z	X	Y	Z
A	0.247	0.636	0.031	6.46	5.68	0.61
B	0.233	0.498	0.061	6.10	4.45	1.20
C	0.220	0.498	0.126	5.76	4.45	2.46
D	0.201	0.358	0.158	5.26	3.20	3.09
E	0.198	0.222	0.114	5.18	1.98	2.23
F	0.176	0.089	0.144	4.61	0.80	2.82
G	0.158	0.965	0.094	4.13	8.62	1.83
H	0.163	0.975	0.022	4.27	8.71	0.42
I	0.196	0.095	0.006	5.12	0.85	1.20
J	0.210	0.225	0.044	5.49	2.01	0.86
K	0.234	0.358	0.022	6.12	3.20	0.43
A'	0.008	0.114	0.162	0.22	1.02	3.17
B'	-0.014	0.253	0.132	-0.38	2.26	2.58
C'	-0.066	0.253	0.095	-1.74	2.26	1.85
D'	-0.088	0.392	0.067	-2.29	3.51	1.30
E'	-0.056	0.525	0.069	-1.45	4.69	1.35
F'	-0.071	0.645	0.022	-1.86	5.76	0.43
G'	-0.033	0.765	0.014	-0.87	6.84	0.27
H'	0.019	0.765	0.050	0.49	6.84	0.97
I'	0.038	0.637	0.093	1.00	5.69	1.83
J'	0.000	0.522	0.107	0.00	4.66	2.10
K'	0.012	0.392	0.142	0.31	3.51	2.78
A"	0.067	0.117	0.198	1.76	1.05	3.87
B"	0.092	0.253	0.234	2.40	2.26	4.58
C"	0.148	0.253	0.277	3.87	2.26	5.42
D"	0.175	0.392	0.307	4.58	3.51	6.00
E"	0.145	0.531	0.298	3.79	4.75	5.83
F"	0.166	0.665	0.339	4.34	5.94	6.63
G"	0.136	0.793	0.342	3.56	7.09	6.69
H"	0.085	0.790	0.301	2.21	7.06	5.89
I"	0.061	0.656	0.257	1.60	5.86	5.03
J"	0.091	0.533	0.249	2.38	4.77	4.87
K"	0.060	0.395	0.211	1.58	3.53	4.13

the axial lengths a, b and c. Co-ordinates in the absolute values of Angstrom units are given under X, Y and Z. Only the carbon atoms of the asymmetric crystal unit (one and a half chemical molecules) are given, the co-ordinates of the other carbon atoms in the unit cell being related to these by the symmetry of space group A2/a.

The state of refinement of the structure does not permit the obtaining of accurate bond lengths. It is possible nevertheless to measure at least approximately the closest approach of non-bonded carbon atoms in the molecule. The measurement can be made on both parts of the asymmetric unit. In the molecule in the general position the distance is 3.1 A. In the molecule in the special position the distance is 2.9 A. The accuracy of these measurements is possibly $\pm$ 0.2 A. The distortion of the molecules (Figure 10) causes atoms G and H to be displaced approximately 1.4 A. and 1.7 A. respectively from a planar configuration.

As required by the symmetry of the space group the molecule in the special position lies with its two-fold axis perpendicular to the (010) plane. The two-fold axis of the molecule in the general position is tilted

a few degrees from perpendicularity.

The compound is a synthetic product and contains the two optical isomers in equal proportions. The two isomers present in the unit cell are related by the glide plane element of symmetry.

A rough measurement may be made of the closest approach between atoms in neighbouring molecules. Between the pair of molecules related by a centre of symmetry and being in the general position the distance between carbon atom G of one and B of the other is 3.4 A. Between H and C of the same molecules is also 3.4 A. The distances between F and D of a molecule in the special position and C of the nearest one in the general position are both 3.2 A. Between H (special) and D (general) is 4.0 A. Between the other pair of molecules in the general position approaches of 3.5 A. (G-E), 3.6 A. (G-F) and 3.3 A. (H-E) are found. These distances are shown in Figure 10.

Discussion

The structure analysis has stopped at a stage of refinement much short of that usually attained in the investigation of aromatic hydrocarbons. By more work

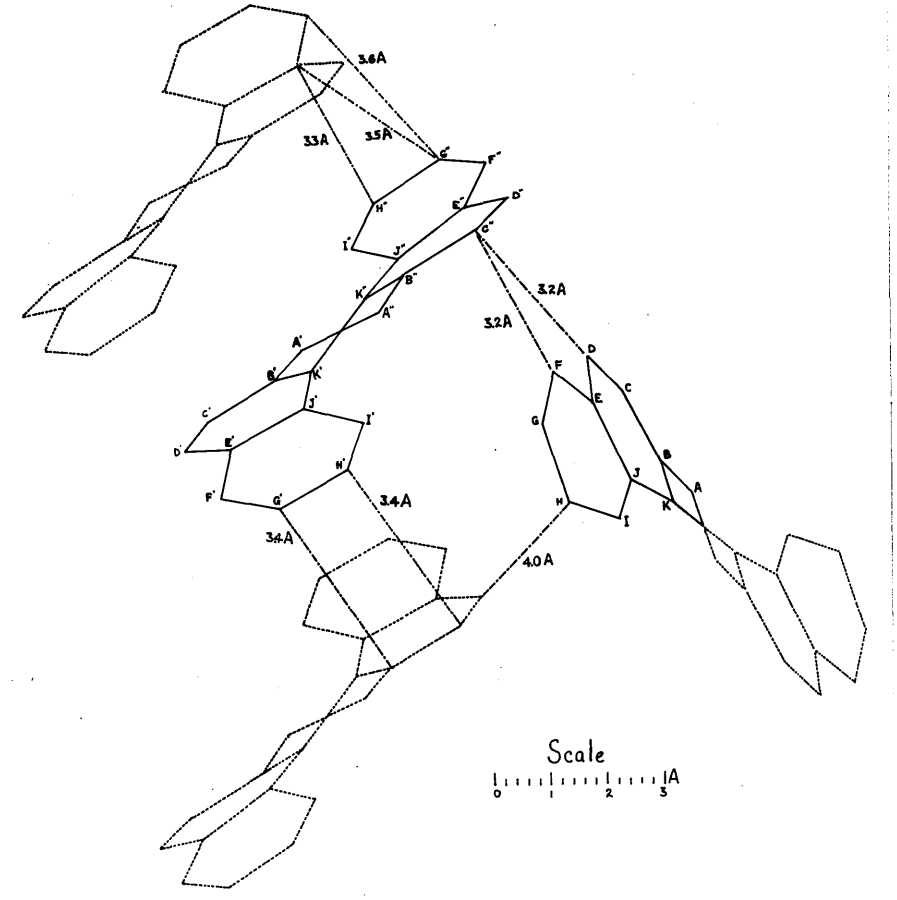

Figure 10. Intermolecular distances in dibenzphenanthrene. The asymmetric unit is shown in full lines.

the discrepancy could be reduced further but it is not likely that by two-dimensional methods it can be brought below 20%.

In spite of this limitation the determination gives a general description of the distortion of the molecule. The type of distortion is the logical one but the amount of departure of an aromatic hydrocarbon from a planar configuration is surprising. Since the molecule is formed during a reaction which produces also an undistorted compound it cannot be under great strain. This may be explained by the fact that the bending is distributed over five fused rings. In the cis-azobenzene molecule (15) the closest approach of non-bonded carbon atoms is 3.3 A. In this case however the resistance to distortion would be less than with dibenzphenanthrene.

During the analysis of the structure two relatively new methods were tried; the technique of the X-ray analogue computer of Pepinsky and the method of difference syntheses.

The computer did not lead to a solution of the problem but it did provide a Fourier projection showing the molecular distortion. The main difficulty was the superposition of atoms in the projection. It is doubtful

if, even with all the signs of the Fourier correct, it would have been possible to choose accurate co-ordinates.

Differences syntheses assisted greatly in the refinement of the (h0l) zone. But here too the overlapping of projected atoms limits the method. In the present problem the large number of co-ordinates to be treated added further to the difficulties. The number of terms in the difference synthesis was not sufficiently large in comparison to the number of atoms in the asymmetric unit. This is probably the cause of the spurious peaks observed in the syntheses.

When the structure determination was well advanced it was learned that 3.4;5.6 dibenzphenanthrene exists in two crystalline forms.(28). The other one is of space group $P2_1/a$ with four molecules in the unit cell. It is rather an unfortunate fact that the form attempted was the more complex. As the supply of the material was not large and there were well formed crystals no attempts at recrystallization were made. If the problem is to be investigated further by triple Fourier methods the simpler space group makes the second modification the obvious subject for the research. The knowledge of the nature of the distortion should aid in the study.

Table 2. Values of the measured and calculated structure factors of 3.4;5.6 dibenzphenanthrene.

hkl	2 sin θ	F_{meas}	F_{calc}
200	0.122	66	91
400	0.244	84	110
600	0.368	60	44
800	0.488	138	-112
10,00	0.610	26	-16
12,00	0.731	107	119
14,00	0.850	72	91
30,00	1.828	16	12
16,02	1.032	18	2
14,02	0.910	41	-51
12,02	0.793	59	-75
10,02	0.675	83	-87
802	0.560	44	70
602	0.440	193	-167
402	0.329	284	341
202	0.231	137	-93
002	0.163	27	27
$20\bar{2}$	0.180	121	-124
$40\bar{2}$	0.255	124	97
$60\bar{2}$	0.360	155	161
$80\bar{2}$	0.470	7	-6
$10,0\bar{2}$	0.590	69	88
$12,0\bar{2}$	0.701	15	3
$14,0\bar{2}$	0.821	55	-45
$26,0\bar{2}$	1.547	23	37
18,04	1.226	16	-15
16,04	1.110	28	1
14,04	0.992	80	-84
12,04	0.880	23	27
10,04	0.769	149	-133
804	0.661	82	-117
604	0.555	148	-127
404	0.461	153	115
204	0.383	88	-87
$00\bar{4}$	0.327	15	23
$20\bar{4}$	0.320	22	46
$40\bar{4}$	0.350	294	-334

hkl	2 sin θ	F_{meas}	F_{calc}
$60\bar{4}$	0.420	272	-265
$80\bar{4}$	0.510	26	26
$10,0\bar{4}$	0.611	14	1
$12,0\bar{4}$	0.718	< 6	5
$14,0\bar{4}$	0.826	61	52
$16,0\bar{4}$	0.941	20	-48
$18,0\bar{4}$	1.059	60	-68
18,06	1.315	37	-37
16,06	1.200	38	30
14,06	1.089	43	-22
12,06	0.986	18	15
10,06	0.882	33	-17
806	0.785	34	50
606	0.690	69	99
406	0.606	9	-3
206	0.543	8	-33
006	0.490	16	30
$20\bar{6}$	0.475	174	-173
$40\bar{6}$	0.486	117	87
$60\bar{6}$	0.528	203	171
$80\bar{6}$	0.595	51	-4
$10,0\bar{6}$	0.673	61	74
$12,0\bar{6}$	0.761	13	14
$14,0\bar{6}$	0.864	23	-8
$16,0\bar{6}$	0.969	21	15
$18,0\bar{6}$	1.076	43	27
$20,0\bar{6}$	1.187	20	--
$32,0\bar{6}$	1.880	20	-16
18,08	1.416	31	-17
16,08	1.315	25	-18
14,08	1.201	16	-23
12,08	1.108	< 8	-9
10,08	1.010	21	32
808	0.920	35	28
608	0.839	55	6
408	0.764	91	102
208	0.706	7	-10
008	0.653	25	35
$20\bar{8}$	0.641	6	16
$40\bar{8}$	0.640	73	-34
$60\bar{8}$	0.668	74	78
$80\bar{8}$	0.710	< 6	-19
$10,0\bar{8}$	0.771	67	85
$12,0\bar{8}$	0.849	15	-5

hkl	2 sin θ	F_{meas}	F_{calc}
14,0$\bar{8}$	0.932	< 7	22
16,0$\bar{8}$	1.025	23	22
30,0$\bar{8}$	1.773	21	22
16,0$\bar{1}$0	1.435	25	27
14,0$\bar{1}$0	1.330	21	2
12,0$\bar{1}$0	1.241	< 9	-4
10,0$\bar{1}$0	1.149	22	-16
8,0$\bar{1}$0	1.060	8	-4
6,0$\bar{1}$0	0.985	11	-13
4,0$\bar{1}$0	0.915	8	2
2,0$\bar{1}$0	0.866	19	-31
00$\bar{1}$0	0.816	16	-10
20$\bar{1}$0	0.800	58	68
40$\bar{1}$0	0.798	97	-81
60$\bar{1}$0	0.810	12	24
80$\bar{1}$0	0.840	112	-121
10,0$\bar{1}$0	0.886	122	-97
12,0$\bar{1}$0	0.948	11	-17
14,0$\bar{1}$0	1.020	< 8	12
26,0$\bar{1}$0	1.585	44	65
16,012	1.550	21	5
14,012	1.455	12	-6
12,012	1.370	14	23
10,012	1.282	< 9	-3
8,012	1.201	24	-37
6,012	1.131	13	20
4,012	1.071	< 8	-17
2,012	1.019	< 8	15
00$\bar{1}$2	0.979	18	-5
20$\bar{1}$2	0.955	33	35
40$\bar{1}$2	0.949	33	-57
60$\bar{1}$2	0.954	< 7	-13
80$\bar{1}$2	0.975	36	-5
10,0$\bar{1}$2	1.010	10	-2
12,0$\bar{1}$2	1.060	40	-47
14,0$\bar{1}$2	1.116	34	-50
18,0$\bar{1}$2	1.263	23	-26
20,014	1.866	16	10
14,014	1.592	9	-19
12,014	1.505	25	-37
10,014	1.430	< 9	2
8,014	1.356	< 9	-2
6,014	1.284	25	31

hkl	2 sin θ	F_{meas}	F_{calc}
4,014	1.228	9	8
2,014	1.182	16	6
00$\bar{1}$4	1.148	<8	10
20$\bar{1}$4	1.120	14	15
40$\bar{1}$4	1.108	12	-39
60$\bar{1}$4	1.108	8	-4
80$\bar{1}$4	1.120	8	-3
10,0$\bar{1}$4	1.149	15	-28
12,0$\bar{1}$4	1.183	58	38
14,0$\bar{1}$4	1.123	42	42
18,0$\bar{1}$4	1.362	38	-27
30,0$\bar{1}$4	1.883	24	-14
10,016	1.580	29	40
8,016	1.506	22	-18
4,0$\bar{1}$6	1.265	13	-11
60$\bar{1}$6	1.263	42	-43
12,0$\bar{1}$6	1.316	40	-36
14,0$\bar{1}$6	1.359	26	-20
20,0$\bar{1}$6	1.535	24	3
28,0$\bar{1}$6	1.856	18	-25
10,018	1.728	16	17
6,018	1.598	44	50
4,0$\bar{1}$8	1.548	30	32
18,0$\bar{1}$8	1.583	24	-7
10,020	1.888	9	12
8,020	1.825	10	-1
2,020	1.675	19	25
00$\bar{2}$0	1.632	32	24
40$\bar{2}$0	1.593	14	-16
80$\bar{2}$0	1.581	13	-31
10,0$\bar{2}$0	1.593	18	12
12,0$\bar{2}$0	1.611	18	1
16,0$\bar{2}$0	1.671	31	10
18,0$\bar{2}$0	1.712	19	19
00 22	1.795	23	-28
020	0.345	56	-56
120	0.350	6	-32
220	0.370	62	-88
320	0.394	64	-22
420	0.425	7	-5
520	0.468	25	-26
620	0.509	33	19

hkl	2 sin θ	F_{meas}	F_{calc}
720	0.557	14	-17
820	0.598	22	16
920	0.650	16	14
10,20	0.700	24	-34
11,20	0.757	10	-2
12,20	0.809	31	43
15,20	0.980	12	18
17,20	1.089	13	--
18,20	1.150	66	75
19,20	1.210	29	30
20,20	1.266	24	12
21,20	1.329	30	1
22,20	1.383	31	27
040	0.690	39	41
340	0.714	29	-26
440	0.730	51	-31
540	0.751	10	15
640	0.780	34	33
740	0.810	10	61
840	0.842	45	59
940	0.882	37	27
10,40	0.919	42	8
11,40	0.962	21	-19
13,40	1.050	22	-9
14,40	1.094	39	43
15,40	1.145	23	-26
16,40	1.194	65	-72
17,40	1.246	14	-32
20,40	1.395	25	10
21,40	1.455	15	28
22,40	1.504	26	10
23,40	1.564	14	-16
25,40	1.679	13	3
26,40	1.728	13	1
30,40	1.950	13	-7
060	1.035	12	-29
260	1.045	38	-48
560	1.080	22	4
660	1.095	13	-35
960	1.170	14	27
10,60	1.195	29	-43
11,60	1.232	14	-35

hkl	2 sin θ	F_{meas}	F_{calc}
12,60	1.268	14	-3
15,60	1.380	25	-1
17,60	1.465	25	-2
18,60	1.508	14	29
080	1.380	97	99
180	1.386	15	18
280	1.380	25	21
380	1.385	31	-28
480	1.393	44	42
580	1.405	25	4
980	1.480	15	-24
10,80	1.502	15	--
11,80	1.526	30	12
0,10,0	1.725	<12	-8
011	0.190	95	-95
013	0.295	51	-46
015	0.445	134	124
017	0.590	33	29
022	0.380	24	30
024	0.470	33	-36
026	0.593	35	-24
033	0.574	35	42
044	0.759	30	-14
046	0.842	94	-110
055	0.950	39	-8
066	1.140	49	-7

The Crystal and Molecular Structure of Decamethylene Glycol

Introduction

This problem was undertaken to obtain further information about the alternation of the carbon-carbon bond lengths in linear aliphatic compounds. Investigation of the dicarboxylic acids (19), and of hexamethylenediamine (4) indicated that there was such an alternation. The differences in the alternate bond lengths, although consistent, were of the same order of magnitude as the experimental errors. The original plan was to determine the structure of decamethylenediamine, a homologue of hexamethylenediamine. The intensity data obtained from the crystals of decamethylenediamine were unsuited for the determination of accurate bond lengths. It was therefore decided to replace the above diamine by the corresponding glycol. The crystals of the latter were better suited to X-ray work. The compound was structurally very similar to the diamine differing only in the substitution of hydroxyl for amine groups. Its chemical properties would be different however. In

addition the glycols had not to our knowledge been investigated by X-ray methods.

The material employed in the study was obtained from L. Light and Company, Limited.

Crystal Data

Decamethylene glycol, $C_{10}H_{22}O_2$; M, 174.3; m.p. 71.5°C; d calculated 1.043, found 1.057. Monoclinic prismatic, $a = 21.52 \pm 0.10$ A., $b = 5.21 \pm 0.03$ A., $c = 4.99 \pm 0.03$ A., $\beta = 97.1 \pm 0.3°$

Absent spectra, (h0l) when h is odd and (0k0) when k is odd. Space group, C_{2h}^5 - $P2_1/a$. Two molecules per unit cell. Molecular symmetry, centre. Volume of the unit cell = 555.1 A^3. Absorption coefficient for X-rays ($\lambda = 1.542$ A.) $\mu = 6.5$ $cm.^{-1}$. Total number of electrons per unit cell = $F_{(000)} = 196$.

Experimental

The material as obtained was in cleavage fragments varying in size from a few millimeters to less than 0.1 mm. Recrystallization from several solvents resulted only in thin crystals so that the material as supplied was used. Decamethylene glycol does not lend

itself to the cutting of suitably shaped specimens. There is a pronounced cleavage parallel to $(40\bar{1})$. When pressure is applied gliding takes place along this plane. However it was possible to pick out properly shaped fragments.

From visual examination of the cleavage fragments it appeared likely that the cleavage directions would be parallel to crystallographic axes. Specimens were set to rotate about the three edges of the cleavage. The setting was done by trial and error. Oscillation photographs showed that one of the axes was an axis of symmetry. Rotation and zero layer moving film photographs were taken about the three axes. Later it became evident that the long axis chosen was really a diagonal. A shorter axis was then found which gave a β angle nearer to 90°. Copper radiation (λ=1.542 A.) was employed throughout the investigation.

The axial lengths as obtained from rotation photographs are as follows;

$$a = 21.52 \pm 0.10 \text{ A.}$$

$$b = 5.21 \pm 0.03 \text{ A.}$$

$$c = 4.99 \pm 0.03 \text{ A.}$$

The β angle found by triangulation was $97.1 \pm 0.3^{\circ}$.

The crystal is monoclinic.

By flotation in aqueous calcium chloride solution the density was found to be 1.057. The density calculated assuming two chemical molecules per unit cell is 1.043.

When the Weissenberg moving film photographs were indexed the (h0l) reflexions were found to be absent when h was odd and the (0k0) ones when k was odd. This indicates a glide plane of translation a/2 and a two-fold screw axis parallel to the b crystallographic axis. At the beginning of the structure analysis doubt existed regarding the exact space group. Only one of the odd orders of (0k0) is visible and it can be seen only on photographs with long exposures. If this (030) be genuine the space group is P2/a and if spurious it is $P2_1/a$. The latter space group was chosen because it satisfied the intensity data. It was concluded that the space group was effectively $P2_1/a$.

From the relation of the cleavage to the crystallographic axes the cleavage planes were identified as (100), (010) and $(40\bar{1})$. The fragments showed striations parallel to $(40\bar{1})$. Figure 13 is a sketch of a fragment bounded by cleavage surfaces.

The intensity data were obtained from zero layer Weissenberg photographs of crystals rotated about the

three axes. The multiple film technique was used to correlate strong and weak reflexions. The intensities were estimated visually. The Lorentz-polarization correction was applied. The square root of the corrected intensity was taken as the relative observed structure factor assuming the crystal to be ideally imperfect. The intensities were not corrected for absorption.

The cross sections of the crystals employed for intensity determinations are as follows;

Zone	Cross section in mm.
(h0l)	0.2 × 0.4 (weak reflexions)
	0.2 × 0.3 (strong reflexions)
(hk0)	0.6 × 0.7
(0kl)	0.3 × 0.5

The percentage of the theoretically possible reflexions that were observed ($\lambda = 1.542$ A.) and the range of the intensities measured are as follows.

Zone	% Observed	Range of Measurements
(h0l)	55½	5400:1
(hk0)	59	6600:1
(hk0)	69½	2200:1

The Fourier syntheses were calculated using three figure numerical methods (27). The a axis was

divided into 120 divisions and the b and c axes into 30 divisions. The structure factor calculations also were numerical using two figure trigonometric tables.

Analysis of the Structure

In space group $P2_1/a$ there are four general positions. Since there are only two molecules per unit cell it follows that the asymmetric unit must consist of half a molecule. This requires the molecule to be centrosymmetric and to be positioned with its centre of symmetry at a centre of symmetry in the unit cell. It is convenient to choose this at the origin. The contents of the unit cell are related by the four equivalent points; x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2}-x, \frac{1}{2}+y, \bar{z}$; $\frac{1}{2}+x, \frac{1}{2}-y, z$.

An examination of the (h0l) and (hk0) intensity data indicated some conspicuously strong reflexions. $(40\bar{1})$ and all its orders are very strong suggesting that almost all the atoms are contributing the maximum amount to this reflexion. Of the (h00) reflexions only (12,00) and (24,00) are strong. The rest of the series are weak. The reflexion (430) also is strong.

Working with the (hk0) structure factors and using a model with the normal dimensions it was relatively

simple to devise co-ordinates that made only (12,00) and (24,00) strong. The y co-ordinates were then chosen to make (430) strong. At this point it became apparent that the space group P2/a did not satisfy the structure factors whereas the space group $P2_1/a$ did. In this zone the structure factor function is different for the two space groups.

Using these co-ordinates all the (hk0) structure factors that had been observed (86 in number) were calculated. The discrepancy expressed as $100\Sigma||F_m| - |F_c||/\Sigma|F_m|$ was 30%.

The x and y co-ordinates of the carbon and oxygen atoms were refined by two successive Fourier syntheses. In these all five carbon atoms and the oxygen atom were clearly resolved. There was no clear evidence of the presence of hydrogen atoms in this projection. The final discrepancy based on the carbon and oxygen contributions was 19%. In the structure factor calculations the composite scattering curve of hexamethylenediamine (4) was employed, scaled for carbon and oxygen.

The projection of the molecule on the (010) plane is shown in Figure 11.

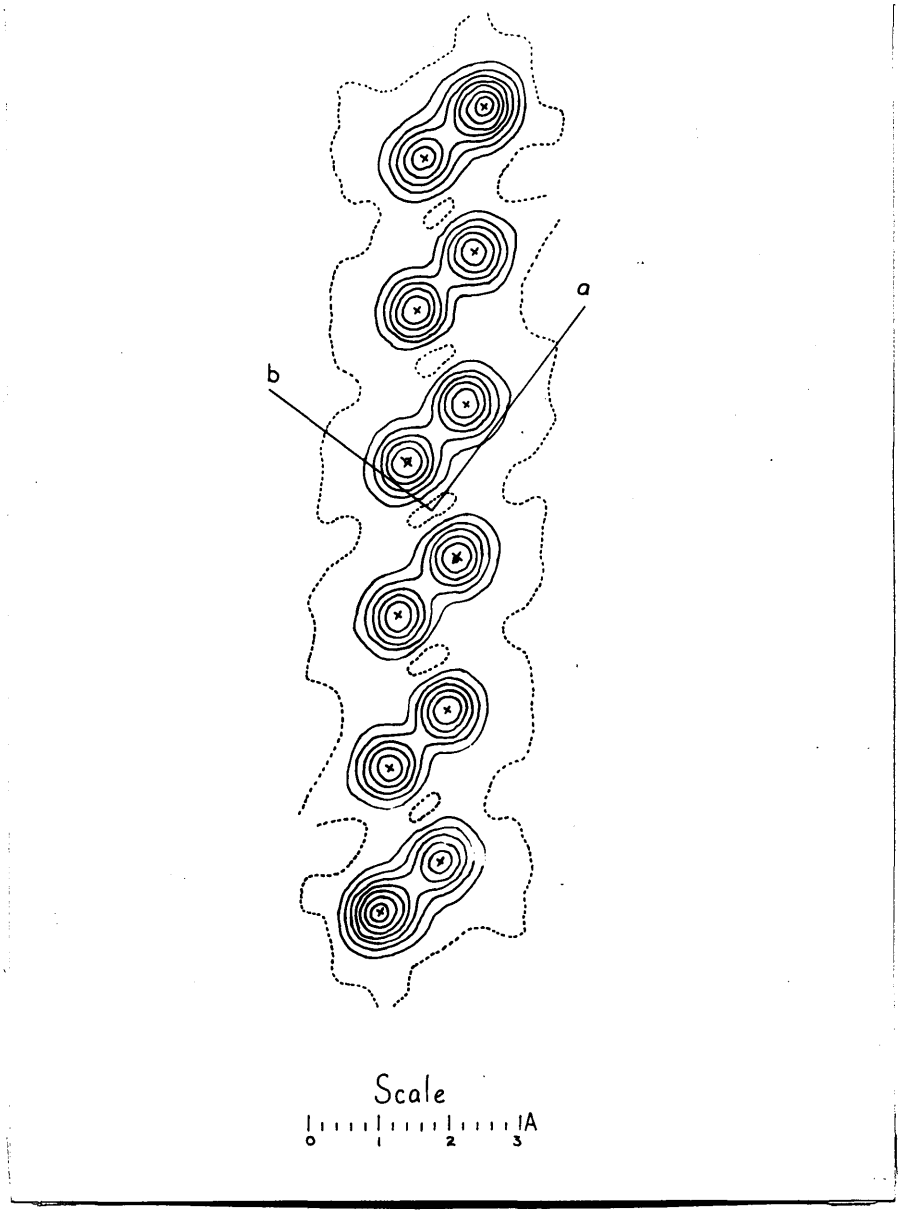

Figure 11. Molecule of decamethylene glycol projected on (001). Contours at intervals of 1 e.Å^{-2}. The one electron line is broken

The strong ($40\bar{1}$) reflexion indicated the molecular position in the (h0l) projection but its high value has caused difficulty in refining the co-ordinates by Fourier methods. The four reflexions ($40\bar{1}$), ($80\bar{2}$), ($12,0\bar{3}$) and ($16,0\bar{4}$) are much more intense than the others in the zone. When the structure factors are calculated the values are found to be much higher than measured. Using a smaller crystal brought up the measured intensity somewhat but it did not correct it completely. Secondary extinction is to be expected when as in this case a structure factor is almost at its maximum value. It is possible too that the temperature factor in this zone is not isotropic since in projection the molecule is viewed edgewise.

To obtain a reasonable Fourier synthesis with the (h0l) data the calculated structure factors for these four reflexions were used instead of the measured ones. In the projection on (0l0) the three pairs of atoms are too close together to give resolution of individual atoms. As a result it was possible to use the projection for the measurement of the z co-ordinates only. These were located with the aid of the x co-ordinates found from the projection on (00l). The z co-ordinates are therefore

less accurate than the x y ones. The projection of the molecule on (010) is shown in Figure 12.

The projection on (010) showed the presence of 20 of the 22 hydrogen atoms. In the projection hydrogen atoms attached to adjacent carbon atoms overlap. The electron density is then sufficient to be observed in the Fourier synthesis. Since the hydrogen atoms contribute 22.5% of the scattering matter an attempt was made to include them in the structure factor calculations. The positions of the hydrogen atoms were calculated assuming a carbon-hydrogen bond of 1.09 A. length. The normal tetrahedral arrangement was assumed. The scattering curve for hydrogen from the sebacic acid analysis (19) was used. The hydrogen contribution was significant only for the (h0l) and (0kl) zones. The inclusion of the hydrogens in the structure factor calculations decreased the discrepancy 3½% in the (h0l) zone, 3% in the (0kl) zone and ½% in the (hk0) zone.

The discrepancies for the three zones are as follows;

hkl	Discrepancy (C,O)	Discrepancy (C,O,H)
(hk0)	18.8%	18.2%
(h0l)	23.5%	20.1%
(0kl)	18.6%	15.8%

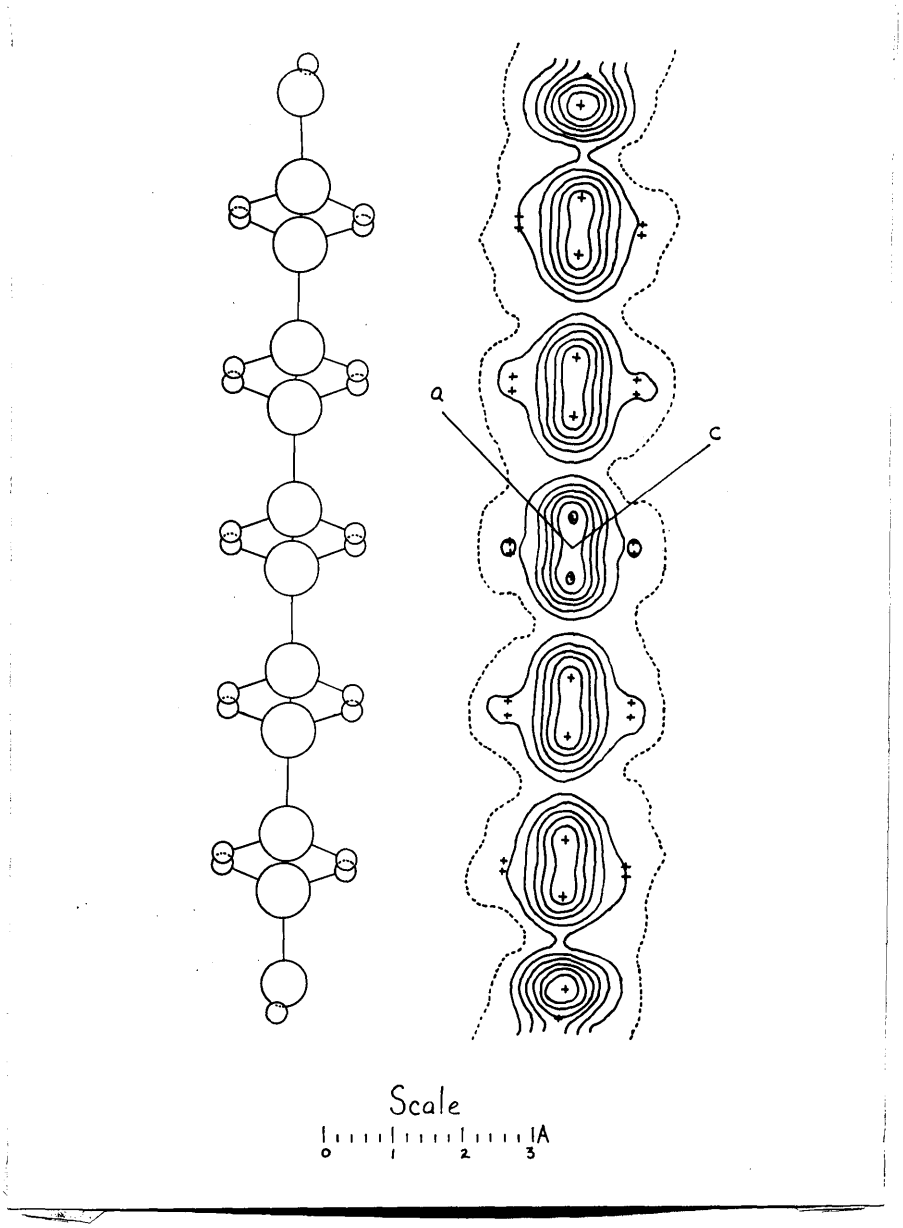

Figure 12. Molecule of decamethylene glycol projected on (010). Contours at intervals of 1 e. A^{-2}. The one electron line is broken. The overlapping of hydrogen atoms is shown in the adjacent diagram.

The four reflexions $(40\bar{1})$, $(80\bar{2})$, $(12,0\bar{3})$ and $(16,0\bar{4})$ have been included in these calculations as having a measured value equivalent to the calculated.

The bond lengths derived from these co-ordinates departed radically from the accepted values. In the (hk0) synthesis the distances C(1)-C(2) , C(3)-C(4) and C(5)-O are much shorter than the intermediate distances. It was the bond lengths between the close lying atoms that were much shorter than normal. It was suggested that the bond lengths might have their unusual values due to the distortion caused by the incompleteness of the Fourier series. To correct for the finiteness of the data the method of Booth (6) was used. This consists in the calculation of a synthesis using the calculated structure factors as coefficients. The co-ordinates from this synthesis are used to correct the ones found with the normal Fourier. The method was shown by Cochran (8) to correct for the finiteness of the series provided that the corrections are small.

The calculation was made for the (hk0) zone using the final set of structure factors. The electron density map obtained was almost identical to that of the corresponding Fourier as shown in Figure 11. The

corrections were never more than 0.02 A. The structure factors were then recalculated using the corrected co-ordinates. It was necessary also to change slightly the co-ordinates of the hydrogen atoms. The discrepancy from the corrected co-ordinates is as follows;

Zone	Number of Reflexions	Discrepancy
(hk0)	86	18.5%
(h0l)	67	22.1%
(0kl)	20	14.7%

Included in the structure factor calculation is the contribution of the hydrogen atoms. The over all discrepancy is 19.7%. In these calculations ($40\bar{1}$) and its higher orders were included as the calculated values. If the actual discrepancy for these planes is used the over all discrepancy becomes 26.3%. The structure factors of the non-observed planes also have been calculated. In this case the hydrogen contributions have not been computed. The structure factors are listed in Table 8.

Co-ordinates, Dimensions and Orientation

The co-ordinates x, y and z of the carbon and oxygen atoms are expressed as fractions of the unit cell edges a, b and c. The absolute values in Angstrom units are listed also as X, Y and Z. These are given only for the asymmetric crystal unit. The other atoms in the unit cell

are related to this by the equivalent points of space group $P2_1/a$. The origin is at a centre of symmetry. The co-ordinates are listed in Table 3.

Table 3. Co-ordinates of the carbon and oxygen atoms.

Atom	x	y	z	X	Y	Z
C(1)	0.014	0.130	0.061	0.306	0.678	0.302
C(2)	0.070	0.092	0.269	1.510	0.480	1.340
C(3)	0.099	0.356	0.384	2.132	1.856	1.916
C(4)	0.154	0.328	0.601	3.316	1.710	2.998
C(5)	0.182	0.589	0.718	3.922	3.068	3.580
O	0.234	0.544	0.906	5.034	2.834	4.522

In Table 4. are listed the analogous co-ordinates for the hydrogen atoms. These values are dependent upon the positions of the carbon and oxygen atoms.

Table 4. Co-ordinates of the hydrogen atoms.

Atom	x	y	z	X	Y	Z
H(1)	0.030	0.237	-0.111	0.644	1.236	-0.551
H(2)	-0.022	0.237	0.142	-0.466	1.236	0.710
H(3)	0.106	-0.015	0.187	2.283	-0.078	0.931
H(4)	0.055	-0.015	0.439	1.173	-0.078	2.193
H(5)	0.114	0.463	0.217	2.452	2.414	1.083
H(6)	0.062	0.463	0.470	1.342	2.414	2.345
H(7)	0.191	0.221	0.516	4.103	1.152	2.575
H(8)	0.139	0.221	0.769	2.994	1.152	3.837
H(9)	0.198	0.696	0.545	4.265	3.626	2.721
H(10)	0.147	0.696	0.798	3.155	3.626	3.982
H(11)	0.245	0.368	0.972	5.278	1.917	4.851

When the co-ordinates of the carbon and oxygen atoms are expressed as the rectangular co-ordinates X', Y and Z' where $X' = X + Z \cos\beta$ and $Z' = Z \sin\beta$ the following values are obtained;

Atom	X'	Y	Z'
C(1)	0.269	0.678	0.300
C(2)	1.344	0.480	1.330
C(3)	1.895	1.856	1.901
C(4)	2.945	1.710	2.976
C(5)	3.479	3.068	3.553
O	4.475	2.834	4.487

From these are obtained bond lengths and valency angles. For comparison the corresponding values before correction for termination of series error are also given.

Bond 5. Bond lengths and valency angles.

Bond	Corrected	Uncorrected
C'(1)-C(1)	1.58 A.	1.58 A.
C(1)-C(2)	1.50 A.	1.46 A.
C(2)-C(3)	1.59 A.	1.61 A.
C(3)-C(4)	1.51 A.	1.45 A.
C(4)-C(5)	1.57 A.	1.58 A.
C(5)-O	1.39 A.	1.35 A.

Angle	Corrected	Uncorrected
C'(1)C(1)C(2)	113°	115°
C(1)C(2)C(3)	112°	115°
C(2)C(3)C(4)	114°	116°
C(3)C(4)C(5)	115°	115°
C(4)C(5)O	110°	111°

The dimensions of the molecule are shown in Figure 14.

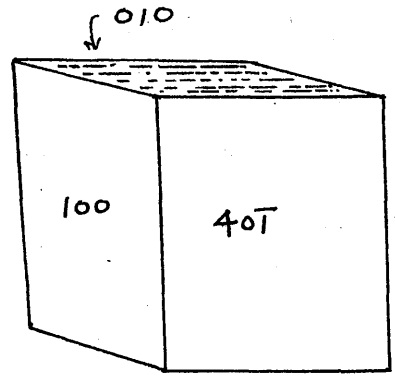

Figure 13. Sketch of a cleavage fragment of decamethylene glycol

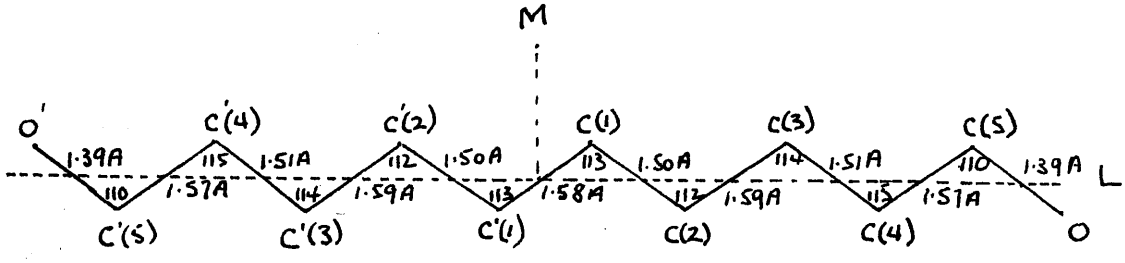

Figure 14. Dimensions of the molecule of decamethylene glycol

In view of the size of the discrepancy it is not likely that the accuracy of the bond lengths is better than 0.03 A. or the valency angles better than 3° to 4° .

The molecules are arranged in layers cutting the c crystallographic axis. The closest approach between neighbouring oxygen atoms is 2.83 A. This hydrogen bonding links the molecules in infinite sheets. The intermolecular distances are greater between molecules in adjacent layers than between molecules in the same layer. Between molecules in the same layer the distances of closest approach are C(1)-C'(1)= 3.94 A., C(3)-C(2) = 3.92 A. and C(5)-C(4) = 3.93 A. The arrangement of molecules in a layer is shown in Figure 15. The hydrogen bridges are denoted by broken lines.

The closest approach of atoms in adjacent layers were;

C(1)-C(3)	4.20 A.
C(1)-C(4)	4.13 A.
C(2)-C(4)	4.17 A.
C(3)-C(5)	4.15 A.
C(3)-O	4.10 A.

The atomic co-ordinates can be referred to molecular axes L, M and N as indicated in Figure 14. The three

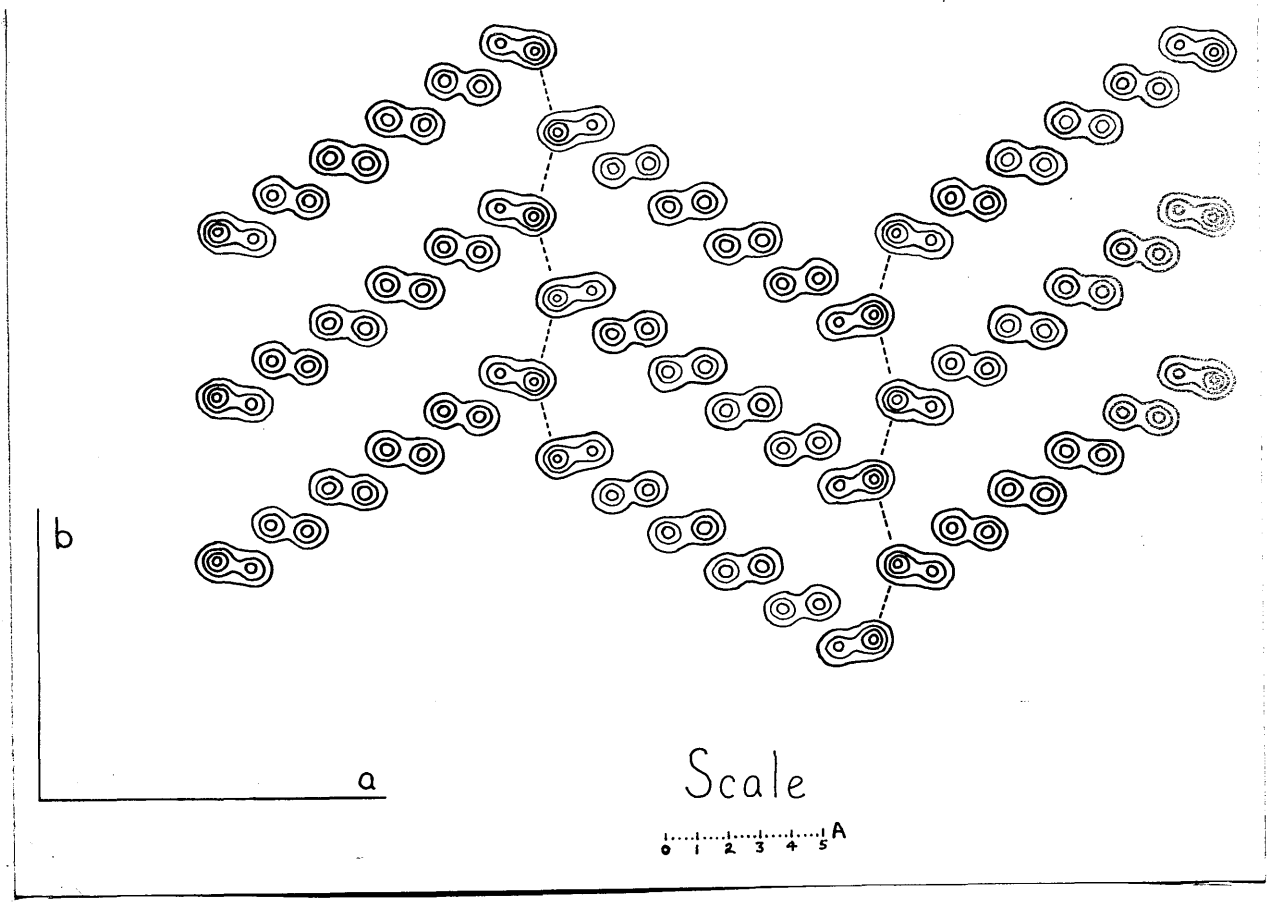

Figure 15. Nine molecules of decamethylene glycol projected on (010). Hydrogen bonds are shown by broken lines.

axes are mutually perpendicular. These values are given in Table 6.

Table 6. Co-ordinates referred to molecular axes.

Atom	L(A)	M(A)	N(A)
C(1)	0.670	0.416	-0.020
C(2)	1.898	-0.447	0.019
C(3)	3.238	0.407	0.007
C(4)	4.505	-0.417	-0.004
C(5)	5.828	0.426	-0.029
O	6.930	-0.412	0.021

The orientation of the molecular axes with respect to the orthogonal crystal axes a, b and c' is given by the following angles;

Table 7. Orientation of the molecule

Loa	51° 14'	Moa	108° 57'	Noa	-44° 42'
Lob	62° 30'	Mob	-27° 30	Nob	90° 00
Loc'	50° 51'	Moc'	109° 15'	Noc'	135° 18'

Discussion

The interatomic distances in decamethylene glycol have been obtained from two syntheses differing greatly in the degree of resolution. This has resulted in one co-ordinate of the atoms being determined with lower accuracy.

The mean difference between alternate carbon-carbon bonds is 0.07 A. This is larger than the estimated error of the measurements and probably is significant. There is

a notable difference between the structure of decamethylene glycol and that of hexamethylenediamine. The long and short bonds occupy different relative positions. In hexamethylenediamine the terminal carbon-carbon bond is short, in the glycol it is long. The glycol thus resembles the 'even' carbon long chain aliphatic dicarboxylic acids (19).

As can be seen from Table 6. the molecule is, within the error of the measurements, planar. The carbon-oxygen bond is shorter than the usual value of 1.42 A.(20). The hydrogen bonds are longer than the value of 2.69 A. found for pentaerythritol (18).

Table 8. Values of the measured and calculated structure factors of decamethylene glycol.

hkl	2 sin θ	F_{meas}	$F_{calc}(C,O)$	$F_{calc}(C,O,H)$
200	0.146	3.1	-8.5	-5.7
400	0.291	3.9	5.5	4.1
600	0.437	2.8	-3.3	-3.1
800	0.582	1.9	1.6	2.2
10,00	0.728	0.8	0.8	-0.3
12,00	0.873	15.5	19.3	17.8
14,00	1.019	<1.0	-0.4	
16,00	1.165	1.5	-0.8	-0.5
18,00	1.310	1.6	1.5	
20,00	1.456	<1.0	1.3	

hkl	2 sin θ	F_{meas}	$F_{calc}(C,O)$	$F_{calc}(C,O,H)$
22,00	1.603	<1.0	0.3	
24,00	1.748	4.8	-6.7	
26,00	1.893	<0.7	1.3	
110	0.302	3.6	3.6	4.0
210	0.322	23.8	- 29.2	-30.7
310	0.368	40.9	44.4	46.3
410	0.412	21.7	-20.2	-20.1
510	0.470	9.3	-9.5	-8.0
610	0.521	8.6	8.9	9.0
710	0.590	6.9	5.4	5.5
810	0.650	5.1	-4.8	-4.8
910	0.720	6.7	-6.0	-6.2
10,10	0.785	2.0	0.3	0.5
11,10	0.855	4.3	3.1	3.3
12,10	0.922	<0.9	-0.3	
13,10	0.994	1.3	--	-0.3
14,10	1.060	7.2	-8.8	-8.6
15,10	1.130	13.2	14.8	14.6
16,10	1.202	5.9	-6.8	-6.6
17,10	1.275	3.3	-4.2	
18,10	1.345	3.4	4.5	
19,10	1.416	<1.1	2.0	
20,10	1.486	4.1	-6.1	
21,10	1.557	5.8	-7.9	
22,10	1.630	3.2	-3.4	
23,10	1.702	<1.0	0.5	
24,10	1.774	<0.9	0.6	
25,10	1.844	<0.8	--	
26,10	1.917	<0.2	-0.1	
27,10	1.991	<0.2	--	
020	0.592	9.4	12.2	9.6
120	0.599	10.8	-7.7	-7.8
220	0.610	10.8	-11.2	-8.9
320	0.632	11.1	9.2	9.5
420	0.660	11.5	13.3	11.0
520	0.696	19.7	-18.6	-16.0
620	0.733	20.4	-11.0	-15.9
720	0.782	12.3	-13.3	-15.0
820	0.830	1.2	-1.4	-1.8
920	0.885	<0.8	0.8	
10,20	0.938	<0.9	-1.5	
11,20	0.992	<0.9	0.4	
12,20	1.054	<1.0	1.8	
13,20	1.118	<1.0	-1.6	

hkl	2 sin θ	F_{meas}	F_{calc}(C,O)	F_{calc}(C,O,H)
14,20	1.176	1.5	-1.5	-1.6
15,20	1.238	<1.1	2.0	
16,20	1.305	3.3	5.0	
17,20	1.370	10.2	-12.3	
18,20	1.439	<1.1	--	
19,20	1.503	8.6	-9.1	
20,20	1.570	4.0	-4.5	
21,20	1.636	2.9	3.2	
22,20	1.707	1.4	2.2	
23,20	1.775	<0.9	-1.6	
24,20	1.846	<0.8	-1.5	
25,20	1.914	<0.6	0.6	
26,20	1.982	<0.3	0.4	
130	0.890	1.5	2.1	2.2
230	0.900	1.4	-1.5	-1.5
330	0.915	13.7	-12.0	-12.4
430	0.935	23.0	-17.6	-17.9
530	0.960	11.7	-10.1	-10.0
630	0.986	4.2	3.0	3.0
730	1.026	4.9	3.6	3.3
830	1.060	<1.0	-0.1	
930	1.106	6.4	-6.2	-6.2
10,30	1.148	1.5	1.8	1.8
11.30	1.196	3.3	3.8	3.8
12,30	1.247	1.1	-0.9	
13,30	1.298	1.6	-2.4	
14,30	1.352	<1.1	-0.1	
15,30	1.402	3.3	-2.4	
16,30	1.467	6.2	-7.6	
17,30	1.524	5.0	-5.3	
18,30	1.581	<1.1	1.6	
19,30	1.642	5.0	5.7	
20,30	1.708	4.3	-5.5	
21,30	1.770	1.3	1.0	
22,30	1.836	<0.8	0.3	
23,30	1.895	<0.7	--	
24,30	1.964	<0.4	0.1	
040	1.182	14.9	-13.3	-12.5
140	1.182	14.9	-14.4	-13.9
240	1.182	9.4	-7.6	-7.1
340	1.196	<1.0	0.3	
440	1.211	3.3	3.6	3.5
540	1.231	<1.1	-1.0	
640	1.256	1.8	-3.5	

hkl	2 sin θ	F_{meas}	F_{calc}(C,O)	F_{calc}(C,O,H)
740	1.282	<1.1	0.5	
840	1.314	2.0	2.2	
940	1.350	<1.1	0.7	
10,40	1.385	5.4	-5.0	
11,40	1.426	5.4	6.3	
12,40	1.463	5.8	-4.4	
13,40	1.512	1.8	-2.3	
14,40	1.560	<1.1	-0.1	
15,40	1.610	<1.0	-0.3	
16,40	1.662	<1.0	-0.1	
17,40	1.711	<1.0	0.5	
18,40	1.767	<0.9	0.3	
19,40	1.820	<0.8	-0.7	
20,40	1.878	<0.7	-0.4	
21,40	1.930	<0.6	0.2	
22,40	1.992	<0.2	0.2	
150	1.478	4.1	-3.7	
250	1.482	7.6	6.2	
350	1.491	4.1	-3.1	
450	1.503	<1.1	-2.1	
550	1.521	<1.1	1.3	
650	1.539	<1.1	0.9	
750	1.561	<1.1	-0.3	
850	1.588	<1.1	-0.9	
950	1.618	<1.0	0.3	
10,50	1.646	1.8	3.2	
11,50	1.680	1.7	2.2	
12,50	1.718	<1.0	0.5	
13,50	1.756	5.2	-4.7	
14,50	1.796	4.9	5.6	
15,50	1.838	2.2	-1.3	
16,50	1.884	<0.7	-1.6	
17,50	1.927	<0.6	0.5	
18,50	1.978	<0.3	0.2	
060	1.775	<0.9	-0.4	
160	1.771	2.5	-2.2	
260	1.775	<0.9	0.4	
360	1.785	2.4	-2.0	
460	1.796	2.4	-1.5	
560	1.806	<0.8	-1.3	
660	1.821	<0.8	2.4	
760	1.842	4.5	4.0	
860	1.865	4.1	3.1	
960	1.890	<0.7	0.1	

hkl	2 sin θ	F_{meas}	$F_{calc}(C,O)$	$F_{calc}(C,O,H)$
10,60	1.915	<0.6	-0.3	
11,60	1.944	<0.5	0.5	
12,60	1.976	<0.3	--	
26,01	1.960	<0.7	0.4	
24,01	1.818	<1.2	-0.9	
22,01	1.662	<1.6	1.9	
20,01	1.525	8.3	-10.4	
18,01	1.384	2.1	1.2	
16,01	1.240	3.5	-2.8	
14,01	1.100	5.4	3.0	2.8
12,01	0.968	5.6	-2.8	-2.7
10,01	0.823	5.0	1.9	2.0
801	0.694	29.7	22.7	32.9
601	0.567	1.9	1.5	3.1
401	0.455	1.1	-0.4	-1.2
201	0.362	<0.8	-1.3	
001	0.316	<0.7	2.8	
20$\bar{1}$	0.332	3.2	-0.7	-0.4
40$\bar{1}$	0.403	65.0	98.0	103.2
60$\bar{1}$	0.514	9.2	-8.9	-11.1
80$\bar{1}$	0.632	5.1	4.2	6.6
10,0$\bar{1}$	0.755	4.1	-2.5	-4.7
12,0$\bar{1}$	0.891	2.8	2.2	3.9
14,0$\bar{1}$	1.025	<1.5	0.6	
16,0$\bar{1}$	1.172	7.2	13.8	12.6
18,0$\bar{1}$	1.302	<1.7	-1.8	
20,0$\bar{1}$	1.455	<1.7	0.2	
22,0$\bar{1}$	1.595	<1.7	0.6	
24,0$\bar{1}$	1.735	<1.4	-0.3	
26,0$\bar{1}$	1.885	<1.1	-0.3	
24,02	1.928	<0.9	-0.2	
22,02	1.796	<1.3	0.7	
20,02	1.660	<1.6	-1.3	
18,02	1.516	<1.7	2.1	
16,02	1.388	10.9	-13.7	
14,02	1.264	5.8	2.6	
12,02	1.140	6.3	-3.7	-3.9
10,02	1.019	7.1	4.0	4.3
802	0.905	8.4	-4.5	-5.0
602	0.805	8.1	4.5	5.2
402	0.724	21.7	19.5	26.0
202	0.660	1.1	2.0	1.4
002	0.630	1.0	-2.9	-1.6
20$\bar{2}$	0.630	2.6	0.8	-1.4

hkl	2 sin θ	F_{meas}	$F_{calc}(C,O)$	$F_{calc}(C,O,H)$
$40\bar{2}$	0.658	1.2	-0.1	1.3
$60\bar{2}$	0.720	2.8	3.1	-0.5
$80\bar{2}$	0.806	23.3	46.8	40.2
$10,0\bar{2}$	0.912	4.6	-6.0	-6.9
$12,0\bar{2}$	1.022	<1.6	2.5	
$14,0\bar{2}$	1.131	<1.6	-1.7	
$16,0\bar{2}$	1.260	<1.7	2.0	
$18,0\bar{2}$	1.384	1.9	0.5	
$20,0\bar{2}$	1.518	6.1	8.9	
$22,0\bar{2}$	1.644	<1.6	-1.6	
$24,0\bar{2}$	1.790	<1.3	0.6	
$26,0\bar{2}$	1.920	<0.9	--	
22,03	1.956	<0.7	-0.4	
20,03	1.830	<1.2	-0.1	
18,03	1.712	1.6	0.7	
16,03	1.590	1.8	-1.3	
14,03	1.470	2.1	1.7	
12,03	1.364	10.9	-14.3	
10,03	1.262	6.1	3.3	
803	1.173	6.0	-4.1	-3.9
603	1.091	6.1	4.6	4.5
403	1.025	5.8	-5.0	-4.7
203	0.975	5.7	5.4	4.6
003	0.948	7.8	12.0	9.4
$20\bar{3}$	0.940	<1.4	1.5	
$40\bar{3}$	0.956	<1.4	-3.2	
$60\bar{3}$	0.996	2.2	1.8	0.8
$80\bar{3}$	1.050	<1.5	1.0	
$10,0\bar{3}$	1.123	3.8	3.7	3.0
$12,0\bar{3}$	1.209	10.3	26.0	25.7
$14,0\bar{3}$	1.309	<1.7	-4.1	
$16,0\bar{3}$	1.416	<1.7	1.6	
$18,0\bar{3}$	1.520	<1.7	-1.1	
$20,0\bar{3}$	1.640	<1.6	1.3	
$22,0\bar{3}$	1.758	1.5	0.3	
$24,0\bar{3}$	1.886	1.7	4.6	
18,04	1.931	<0.9	-0.3	
16,04	1.820	1.5	0.1	
14,04	1.720	1.8	0.3	
12,04	1.625	<1.6	-1.0	
10,04	1.535	<1.7	0.8	
804	1.456	10.9	-12.7	
604	1.388	3.5	3.4	
404	1.334	3.4	-3.9	

hkl	2 sin θ	F_{meas}	$F_{calc}(C,O)$	$F_{calc}(C,O,H)$
204	1.294	3.4	3.4	
004	1.263	3.3	-4.4	
20$\bar{4}$	1.252	4.1	4.6	
40$\bar{4}$	1.265	4.1	6.6	
60$\bar{4}$	1.288	<1.7	1.2	
80$\bar{4}$	1.325	<1.7	-7.1	
10,0$\bar{4}$	1.382	<1.7	1.6	
12,0$\bar{4}$	1.449	<1.7	-1.0	
14,0$\bar{4}$	1.528	3.4	3.2	
16,0$\bar{4}$	1.612	6.5	13.5	
18,0$\bar{4}$	1.715	<1.4	-2.6	
20,0$\bar{4}$	1.820	<1.3	0.8	
22,0$\bar{4}$	1.917	<0.9	-0.4	
14,05	1.986	<0.3	-0.5	
12,05	1.900	<1.0	0.3	
10,05	1.825	1.5	-0.1	
805	1.752	<1.4	-0.6	
605	1.696	1.8	--	
405	1.648	6.3	-9.3	
205	1.610	<1.6	2.8	
005	1.585	<1.6	-2.8	
20$\bar{5}$	1.575	<1.7	2.7	
40$\bar{5}$	1.575	<1.7	-3.2	
60$\bar{5}$	1.587	2.3	3.5	
80$\bar{5}$	1.618	2.5	3.2	
10,0$\bar{5}$	1.660	<1.6	0.9	
12,0$\bar{5}$	1.710	<1.5	-1.8	
14,0$\bar{5}$	1.775	<1.3	1.2	
16,0$\bar{5}$	1.845	<1.2	-0.8	
18,0$\bar{5}$	1.925	1.4	2.0	
406	1.962	<0.7	-0.1	
206	1.926	1.0	-0.4	
006	1.906	1.4	-5.3	
20$\bar{6}$	1.895	2.4	1.7	
40$\bar{6}$	1.894	<1.1	-1.6	
60$\bar{6}$	1.900	<1.0	1.4	
80$\bar{6}$	1.920	<0.9	-1.7	
10,0$\bar{6}$	1.950	<0.7	1.4	
12,0$\bar{6}$	1.992	<0.3	0.3	
011	0.427	25.1	-23.5	-24.0
012	0.686	5.3	-5.2	-5.0
013	0.978	<0.9	0.7	
014	1.275	8.8	-7.4	

hkl	2 sin θ	F_{meas}	$F_{calc}(C,O)$	$F_{calc}(C,O,H)$
015	1.577	1.1	-2.8	
016	1.890	<0.7	0.3	
021	0.667	10.9	12.6	11.2
022	0.857	4.6	-4.3	-4.3
023	1.101	<1.0	-1.0	
024	1.373	1.1	1.9	
025	1.658	3.0	-5.3	
026	1.958	<0.4	-0.8	
031	0.940	22.7	-18.7	-18.9
032	1.084	1.7	-1.1	-1.1
033	1.288	1.1	-0.9	
034	1.526	5.6	-6.3	
035	1.784	1.8	-3.3	
041	1.218	3.2	3.3	3.2
042	1.331	1.6	2.0	
043	1.502	5.2	-4.9	
044	1.710	<1.0	-0.6	
045	1.948	<0.5	-0.5	
051	1.510	1.9	-2.2	
052	1.602	<1.1	-1.6	
053	1.746	0.9	0.2	
054	1.928	<0.6	-0.3	
061	1.801	1.5	-1.5	
062	1.878	2.6	3.0	

APPENDIX

The Structure of Decamethylenediamine

Introduction

The investigation of hexamethylenediamine (4) indicated an alternation of carbon-carbon bond lengths. The differences between alternate bond lengths were of the same order of magnitude as the experimental error of the measurements. To obtain further information it was decided to investigate the homologue decamethylenediamine. The solution of the problem requires the determination of accurate bond lengths. Experimental difficulties did not permit the obtaining of a sufficient range of accurate intensity measurements and the work has not been completed. However an approximate determination of the structure has been made.

The sample of decamethylenediamine employed was kindly supplied by Imperial Chemical Industries Limited.

Crystal Data

Decamethylenediamine, $C_{10}H_{24}N_2$, M, 172.3; m.p. 61.5°C ; d. calculated 0.937, found 0.88 - 1.04. Orthorhombic dipyramidal,

$a = 7.25 \pm 0.05$, $b = 5.72 \pm 0.03$, $c = 29.4 \pm 0.2$ A

Absent spectra, (h0l) when l is odd, (0kl) when k is odd and (h00) when h is odd. Space group, D_{2h}^{15} - Pbca. Four molecules per unit cell. Molecular symmetry, centre. Volume of the unit cell = 1219 A^3. Absorption coefficient for X-rays (λ 1.542 A.) $\mu = 4.9$ $cm.^{-1}$. Total number of electrons per unit cell = $F_{(000)} = 392$.

Experimental

The material as received was in the form of a fine powder. In the description by Phookan and Krafft (22) decamethylenediamine is reported to be both hygroscopic and an absorber of carbon dioxide. The hygroscopic nature did not prove to be a problem. However the compound quickly changed on exposure to the atmosphere forming a white coating. This is probably the carbonate.

The first part of the problem was the growing of crystals suitable for X-ray work. Numerous organic solvents were employed but the crystals were always too small. Very thin laths were obtained by the slow evaporation of a solution in dilute aqueous sodium hydroxide.

A diffusion method of growing crystals was attempted. In a small test tube was placed about a milliliter of

benzene. On top of this was run a layer of pure isobutyl alcohol. The two liquids did not mix appreciably. Then a solution of decamethylenediamine in isobutyl alcohol was run carefully onto the isobutyl alcohol layer. The tube was then set aside for a few days. The decamethylenediamine is almost insoluble in benzene and in time the benzene diffused into the isobutyl alcohol layer causing crystallization to occur. Thin curved crystals were obtained, the best specimens grown from organic solvents.

An attempt at vacuum distillation of the decamethylenediamine as had been successful with hexamethylenediamine (4) gave only small crystals. The different behaviour of the two compounds is due probably to the difference in volatility.

The best crystals were obtained by sublimation under reduced pressure at 60° - 70° C. These were thin curved blades. Although not appropriately shaped these were used in the investigation.

Later work on the problem included the synthesis of more of the decamethylenediamine using the method of Slotta and Tschesche (29). The starting material was sebacic acid. The diamine was obtained by way of the dichloride, diamide and dinitrile. It had been hoped to

obtain better crystals by the slow decomposition of the dihydrochloride. This did not give suitable crystals. An alternative attempt to grow crystals of the decamethylenediamine dihydrochloride was equally unsuccessful. The chlorine content of this latter compound is sufficiently low to give hope of good resolution of the carbon and nitrogen atoms in Fourier syntheses.

During the taking of X-ray photographs the crystals were enclosed in gelatin capsules containing a small amount of calcium chloride. The crystals were very thin, requiring long exposures. The long exposure, combined with the presence of the gelatin in the X-ray beam caused the films to have a heavy background.

The crystals were set first to rotate about the long axis of the blade. From this rotation photograph an axial length was found. A zero layer Weissenberg moving film photograph was then taken about the same axis.

The next setting was an axis at right angles to the first and in the plane of the blade. This gave another axial length. A zero layer Weissenberg photograph also was taken about this axis. Oscillation photographs indicated that both axes were symmetry axes.

The third axis of the crystal is perpendicular

to the plane of the blade of the crystal. This is a long axis and it was not found possible to set a crystal to rotate about it. A long exposed oscillation photograph was the only direct evidence of this axis. This gave an approximate value however and aided by the moving film photograph the axis was identified. It was measured from a b axis rotation photograph using the (00,24) reflexion.

The interaxial angles were measured on the moving films and were found to be 90°. The axial lengths are;

$a = 7.25 \pm 0.05$, $b = 5.72 \pm 0.03$, $c = 29.4 \pm 0.2$ A.

The b axis is the long axis of the blade. The crystal is orthorhombic. When the Weissenberg photographs were indexed it was found that (h0l) reflexions were absent when l was odd, (0kl) when k was odd and (h00) when h was odd. The failure to obtain a zero layer moving film about the long axis prevented the inspection of the (hk0) reflexions. The data indicate glide planes of translation b/2, c/2 and possibly a/2. The orthorhombic space group having these symmetry relations is D_{2h}^{15} - Pbca.

By the flotation method the density was found to lie between 1.04 and 0.88. The calculated density for four molecules per unit cell is 0.937.

The intensity data were obtained from zero layer Weissenberg photographs taken of crystals rotated

about the a axis. Copper radiation (λ=1.542 A.) was employed throughout the experimental work. The multiple film technique was used to correlate strong and weak reflexions. The intensities were estimated visually. Due to the unsuitable crystals and the heavy background only 25 reflexions out of a possible 112 were observed. The intensities were corrected by the Lorentz-polarization factor. No absorption correction was applied. The accuracy of these measured structure factors is not high.

The only synthesis calculated during the investigation employed three figure numerical methods. For the calculation the c axis was divided into 120 divisions and the short b axis into 30 divisions.

Analysis of the Structure

The analysis was not completed but considerable progress was made.

In the space group Pbca there are eight general positions. The unit cell contains only four molecules so that the asymmetric unit must be half the chemical molecule. This implies that the molecule be centrosymmetric and be positioned at a centre of symmetry in the unit cell. It is convenient to choose this as the origin. It is to be noted that hexamethylenediamine

possessed similar symmetry.

A comparison of the axial lengths of decamethylenediamine and hexamethylenediamine (4) show a marked similarity.

Axis	Decamethylenediamine	Hexamethylenediamine
a	7.25 A.	6.94 A.
b	5.72 A.	5.77 A.
c	29.4 A.	19.22 A.

Both compounds are of space group Pbca. If allowance be made for the increased length of the decamethylenediamine molecule the two unit cells are almost equivalent. It therefore seemed reasonable to start from the orientation found for the hexamethylenediamine molecule. The (0kl) zone of reflexions were the only ones dealt with. However it was noted that the (200) reflexion was extremely strong. This was taken to indicate that in projection the long axis of the molecule lay parallel to the c crystallographic axis. In the case of hexamethylenediamine the same reflexion was very strong.

Using the hexamethylenediamine orientation as a starting point and after many trials a reasonable fit was found between measured and calculated structure factors from the (0kl) zone. In the final trial structure all the

bond lengths were assumed to be 1.54 A. and the valency angles to be 115°. The structure factor calculation did not include the contribution of the hydrogen atoms which in this case make up 24.5% of the scattering matter. The discrepancy calculated in the usual manner was 36%. There were only 25 structure factors included in the calculation.

A Fourier synthesis was now computed for this zone. This is shown in Figure 16. All the carbon and the nitrogen atoms are resolved but the outlines are angular.

From the plot of the electron density new co-ordinates for y and z were chosen. From these the structure factors were recalculated. The discrepancy decreased to 34%. None of the structure factors changed sign. No further attempt was made to refine the structure.

Co-ordinates

Since the structure has not been refined it cannot be claimed that the following co-ordinates are more than tentative. In the values listed y and z are expressed as fractions of the axial lengths b and c. Y and Z are the absolute values of the co-ordinates in Angstrom units. Only the values of the atoms in the asymmetric unit are given the co-ordinates of the other atoms in the unit cell being obtained from the relations applicable to space group

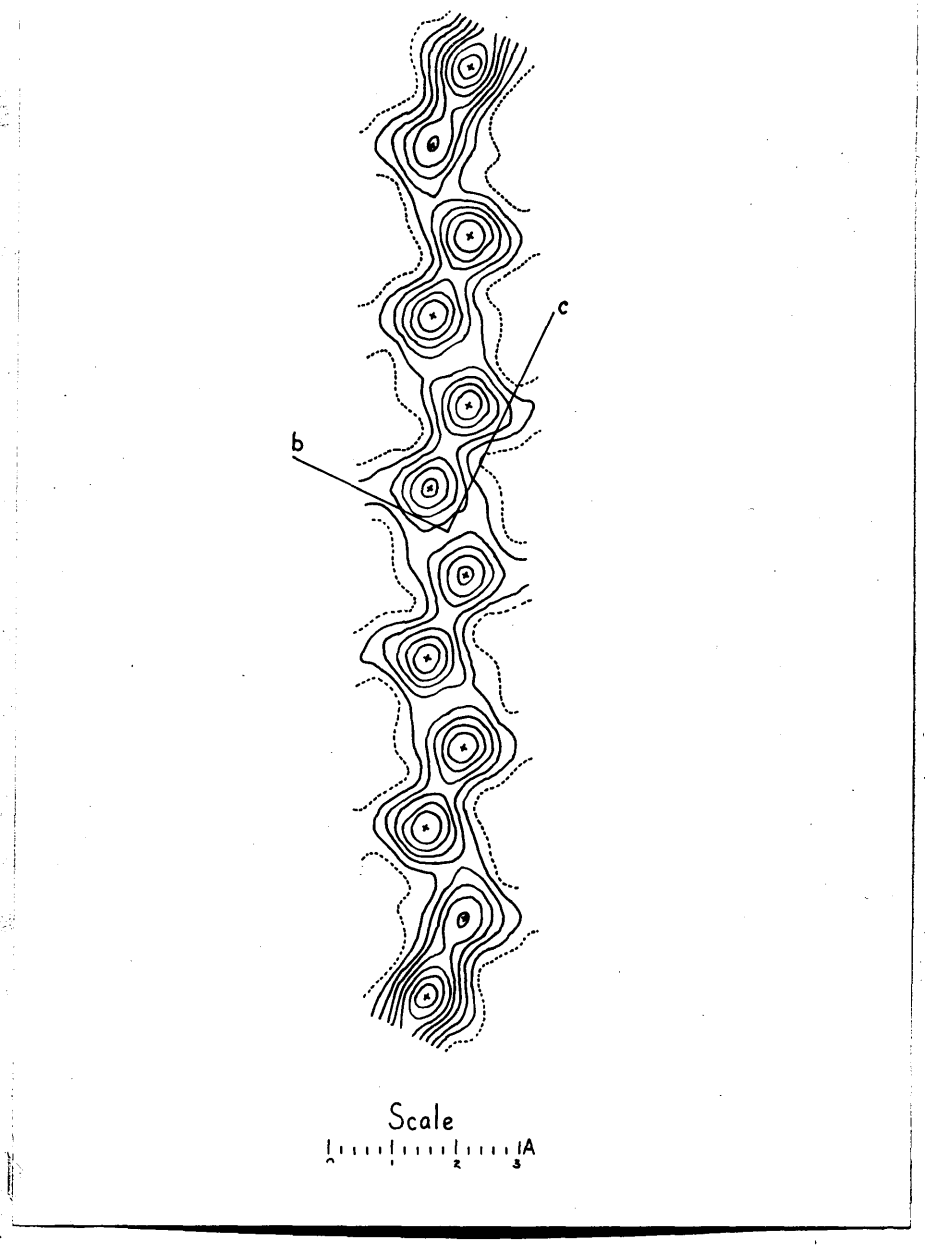

Figure 16. Molecule of decamethylenediamine projected on (100). Contours at intervals of 1 e. A^{-2}, the one electron line being broken.

Pbca;

$x,y,z;\ \frac{1}{2}+x,\frac{1}{2}-y,\bar{z};\ \bar{x},\frac{1}{2}+y,\frac{1}{2}-z;\ \frac{1}{2}-x,\ \bar{y},\frac{1}{2}+z;$

$\bar{x},\bar{y},\bar{z};\ \frac{1}{2}-x,\frac{1}{2}+y,z;\ x,\frac{1}{2}-y,\frac{1}{2}+z;\ \frac{1}{2}+x,\ y,\frac{1}{2}-z.$

Table 9. Co-ordinates obtained from projection on (100)

Atom	y	z	Y	Z
C(1)	0.123	0.022	0.70	0.64
C(2)	0.128	0.085	0.73	2.50
C(3)	0.381	0.130	2.18	3.83
C(4)	0.384	0.191	2.19	5.62
C(5)	0.647	0.235	3.70	6.91
N	0.647	0.295	3.70	8.68

The values of the measured and calculated structure factors are given in Table 10.

Discussion

The main difficulty in the investigation of the structure of decamethylenediamine has been the unfavourable physical character of the crystals. With crystals of the type obtained up to the present it would be extremely difficult to measure accurately a large range of intensities. It was because of the time consuming experimental nature of the problem that work was transferred to the analogous compound decamethylene glycol.

Due to the similarity of the structures of the two homologous diamines there can be little difficulty with the actual analysis of the decamethylenediamine.

Table 10. Values of the measured and calculated structure factors of decamethylenediamine.

hkl	2 sin Θ	F_{meas}	F_{calc}
00,12	0.629	57.8	32.0
00,14	0.733	22.4	12.0
00,16	0.839	8.2	-8.1
00,18	0.942	8.9	10.6
00,24	1.259	32.6	-55.1
020	0.538	52.4	36.1
021	0.540	10.6	9.4
022	0.550	56.1	-37.9
023	0.561	10.9	-16.3
024	0.578	100.0	74.1
025	0.604	56.3	-50.8
027	0.652	35.9	-31.7
028	0.681	37.0	-28.1
02,16	0.998	9.3	23.3
02,17	1.043	9.6	-29.6
02,18	1.087	9.9	13.7
02,19	1.136	30.6	-31.7
02,20	1.180	31.3	-43.3
040	1.076	17.1	19.8
041	1.080	9.9	-19.8
042	1.082	29.6	-39.2
043	1.090	17.2	-26.2
061	1.615	10.5	10.2
062	1.617	14.6	-19.5
063	1.620	10.4	11.4

An Attempted Determination of the Cell Dimensions of Naphthalene using the Straumanis Technique

Introduction

This was in the nature of an introductory problem carried out in connection with the three dimensional investigation of the structure of naphthalene (1).

Refined methods for the determination of bond distances in molecules by the X-ray method require that the unit cell constants be known with an accuracy greater than that obtained from the usual rotation photograph. With the latter method the axial lengths are not more accurate than ± 0.02 A. Much higher accuracy has been reported with the Straumanis technique (30,31,32). This has been used both with powdered and with single crystal specimens. A small specimen is used to reduce absorption and refraction effects. The circular film is so mounted that reflexions from both the high and low angle regions on both sides of the X-ray beam are registered on the same film. In this manner reflexions at low and high values of $2\theta = 180-A$ will be accompanied by the equivalent reflexion at $2\theta = 180+A$. This asymmetrical mounting permits an accurate measurement of the ingoing and outgoing positions of the X-ray beam (the position of

$2\theta = 180^\circ$ and of $2\theta = 0^\circ$). Thus the effective radius of the camera can be found precisely from the same film upon which is recorded the axial reflexion being measured. It is assumed that the film shrinkage will be uniform. For the most precise work it is necessary to maintain the X-ray camera at a constant temperature. A temperature difference of 1°C. makes a measureable change in the fourth decimal place of the axial lengths. The Straumanis technique in the past has been applied to metals and other inorganic substances that give strong reflexions in the high angle region. It is recommended that the reflexion used for the measurement should lie between $\theta = 80^\circ$ and $\theta = 90^\circ$.

In applying the technique to naphthalene it was planned to use short oscillations to obtain a pair of high order axial reflexions. The value of $2\theta = 0^\circ$ would then be found from a pair of low order reflexions on the same film. By finding the angular values for high orders of the three axial spacings and knowing β the three axial lengths could be calculated. As the oscillation photograph brings only a limited area of the reciprocal lattice into a position of reflexion the high orders would be identifiable. The oscillation also is equivalent to a much longer exposure with a moving film camera.

Experimental

Crystals were obtained by allowing a methanolic solution of naphthalene to evaporate slowly. From morphological data (38) it was possible to identify the a and b crystallographic axes. The final setting was by trial. The specimens were protected from evaporation by enclosing them in gelatin capsules containing some naphthalene (1). By identification of low order reflexions on the oscillation pattern it was possible to find the orientation of the crystal. The position of high order axial reflexions could then be calculated using Bragg's law. The reported axial reflexions are listed below (1,23).

hkl	F_{meas}	θ (Cu K_α)
200	43.9	12° 47'
400	4.6	26° 10'
600	6.2	41° 27'
800	1.3	61° 53'
020	14.7	14° 46'
040	0.8	30° 40'
060	<1.6	49° 54'
001	33.5	6° 5'
002	18.2	12° 11'
003	22.4	18° 29'
004	16.5	24° 58'
005	1.6	31° 52'
006	2.7	39° 17'
007	3.9	47° 39'
008	1.3	58° 00'
009	<1.4	72° 33'

There seemed to be little possibility of obtaining a high order axial reflexion in the region of $\theta = 80^{\circ}$. However (007) was located and measured. In order that the full accuracy of the Straumanis method be obtained it is necessary that the film be measured with a tolerance of 0.01 mm. This was attempted with a travelling microscope but the spot could not be distinguished from the background. Longer exposures did not improve the visibility of the reflexion. Finally the position of the spot was marked with a fine mapping pen and the ink mark was measured. When other photographs were measured consistent results were not obtained.

Attempts at locating (060) using long exposures were not successful. At this point the work was suspended.

Discussion

The failure of the method in the case of naphthalene appears to be due to the weakness of the high order axial reflexions. In the applications cited by Straumanis (30,32) inorganic materials such as sodium chloride and aluminium were used. These substances give strong high order reflexions and can be treated by the Straumanis technique. It appears that a method for general use with organic compounds must make use of the forward reflexion area.

Increased accuracy could be obtained by increasing the film to specimen distance and then determining this distance by the use of a standard substance. A recently developed method makes use of a precession camera to obtain an undistorted photograph of the reciprocal lattice.(7) It is reported to have an accuracy intermediate between that of the ordinary rotation pattern and the Straumanis technique (2). It reduces the variation in measurements of axial lengths to the third decimal place. It also permits the direct measurement of the reciprocal angles.

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